S & J ENGINEERING

Final Report

SURVEY OF HYDRODYNAMIC EFFECTS WITH MACROMOLECULES

A. LOW REYNOLDS NUMBER FLOW THROUGH MATRICES OF FINE STRANDS
B. DYNAMICS OF LONG CHAIN POLYMERS IN FLOWING SOLVENTS
C. FLOW OF POLYMER SOLUTIONS IN POROUS MEDIA
D. HYDRODYNAMIC EFFECTS OF POLYMERS IN FLOCCULATION
E. FEASIBILITY STUDY AND DEVELOPMENT OF A FIRST MODEL OF A SETTLING VELOCIMETER

by

David F. James, Ph.D., P.Eng.

Work Conducted for the Department of Energy, Mines and Resources

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Organization of Final Report

This final report is a compilation of five separate reports. The first four are literature surveys on different but related topics and the last is the report of the development of a settling velocimeter. Each constituent report is self-contained, mainly because three of the surveys were submitted individually during the work. Each report, accordingly, has its own title page, table of contents, numbering system and bibliography, and can be read entirely on its own.

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A. LOW REYNOLDS NUMBER FLOW THROUGH MATRICES OF FINE STRANDS

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LOW REYNOLDS NUMBER FLOW THROUGH MATRICES OF FINE STRANDS

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1. INTRODUCTION

1.1 Purpose and Search Technique

This review was undertaken with a particular porous medium in mind: a randomly-circled macromolecule in solution or entangled macromolecular chains in solution. An overall purpose in our research program is to determine hydrodynamic forces on polymer chains and one way of treating the problem is to consider the loosely-wound macromolecule as a porous medium. This approach is used, for example, in sedimentation tests to relate the molecular weight of a polymer sample to its sedimentation coefficient. Yet this technique does not determine the hydrodynamic forces on a coil nor the effective permeability of the coil. For a single macromolecule, such knowledge would be useful. for instance, in enhanced oil recovery to predict the flow resistance of surface-absorbed or gelled macromolecules, or in rheology to find the deformation of molecule and hence its contribution to the stress field. The purpose of the survey, then, was to search out all the existing theoretical work on strand-type porous media, i.e. media which might represent polymer chains in solution.

The survey was carried out along two separate paths: Graham Jackson found all the references he could by expanding the bibliography of his M.A.Sc. thesis (on the permeability of byaluronic chains) and by using a computer search. Working independently, David James searched the

literature by cross-checking the bibliographies of articles and using the Source and Citation indices. He also contacted leading researchers in the field, which confirmed his knowledge of the latest developments and even led to a significant paper which has not yet appeared in print. The two searches matched very well and so it is unlikely that important papers have been overlooked.

1.2 Elements of Flow Through Porous Media

In this review on theories of flow through porous media, emphasis is placed on media classified as fibrous because such theories may be applicable to entangled polymer molecules. Very little work has been done on this application, and so available theories which have been developed for media like fabric and paper filters, metal gauzes, and fiber glass packs. Although some of the early theoretical work was developed for other types of porous media, the theories are sufficiently general to be applicable to fibrous media as well.

The first law for flow through porous media appears to have been proposed by Darcy (1856). His one dimensional equation, now known as Darcy's Law, was based on experiments with sand beds and takes the form

$$Q/A = Kh/L, \qquad (1)$$

where Q is the flow rate, A is the medium cross sectional area, K is the Darcy constant, and h is the driving head over a length L, the medium thickness. Darcy's Law is a global (or control-volume) law which can be shown to satisfy

the differential equation for fluid motion at each point within the medium. That is, it satisfies Stokes equation,

$$\nabla p = \mu \nabla^2 V, \qquad (2)$$

when the Reynolds number is less than 1.0 (p is the local pressure, μ is the viscosity and V is the superficial velocity, Q/A). At higher Reynolds numbers, the inertial terms of the full Navier-Stokes equation become important, and Stokes equation no longer governs the flow. Examples of flow through porous media which do not obey Darcy's Law or the Stokes equation can be found in high capacity gas and liquid filtering systems. However, for low Reynolds number flow, equation (1) has been shown to hold true for a wide variety of porous media - porous plates (Brunhes, 1924), fine powders (Traxler & Baum, 1936), collodion membranes (Bigelow, 1907) and sands (Fancher & Lewis, 1933) - and is now more commonly written in one dimensional form as

$$V = - (k/\mu)(dp/dx), \qquad (3)$$

or in vector form as

$$\bar{V} = - (k/\mu)\nabla p, \qquad (4)$$

where k is the porous medium hydrodynamic permeability, which is related to the Darcy constant K.

It is the prediction of k, or K, which will be reviewed herein. The permeability k is a function of the size and shape of the fibers, and how the fibers are structured to form the medium. It does not depend on the fluid viscosity, density, or velocity in the regime of low Reynolds number flow.

2. FLOW THROUGH EQUIVALENT TUBES

Another law which satisfies Stokes equation (2) is Poiseuille's Law (1840) for steady laminar flow in a tube of constant cross sectional area. For a circular tube of radius a, the law can be written as

$$V = - (a^2/8\mu)(dp/dx), \qquad (5)$$

where the symbols have the same meaning as in equations (3) and (4). The similarity of Poiseuille's Law to Darcy's Law lead to the first attempts to estimate k for a porous medium. Using a Poiseuille flow analogy, low porosity granular media were visualized as bundles of many small tubes or flow passages. Although passages in real media have interconnections, irregular areas, and varying orientations to the flow direction, it seemed logical to apply equation (5) and determine a relationship between flow rate, pressure gradient and the media structure. The first such attempts were made by Slichter (1897-1898) and by Kozeny (1927). Kozeny developed the following relation

$$V = - (\varepsilon^3/k'\mu S^2)(dp/dx), \qquad (6)$$

where ε is the porosity of the medium expressed as fractional free volume, k' is the Kozeny constant and S is the surface area of particles per unit volume of the medium. The Kozeny constant is related to the hydrodynamic permeability k as follows:

$$k = \varepsilon^3/k'S^2 \quad . \qquad (7)$$

For a packed bed of spheres, Kozeny showed that k' should have a value of 5. Carman (1938) compared experimental data to the Kozeny equation and verified that k' = 5 was valid for spheres, and that for non-spherical particals k' was not significantly different. He also modified equation (6) so that it included the specific surface S_o of the particles forming the media, instead of S. The resulting relation, now known as the Carman-Kozeny equation, is written as

$$V = - (\varepsilon^3/\mu k' S_o^2 (1-\varepsilon)^2)(dp/dx). \qquad (8)$$

Since

$$S = (1-\varepsilon)S_o, \qquad (9)$$

the permeability in this case is

$$k = \frac{\varepsilon^3}{k' S_o^2 (1-\varepsilon)^2} . \qquad (10)$$

The Carman-Kozeny equation was used for granular-type media, but Wiggins et. al. (1939) recognized that the equation was applicable to other types of media and showed experimentally that is was valid for fibrous particles. Fowler & Hertel (1940) modified the Carman-Kozeny equation specifically for gas flow through fibrous porous media. Their equation includes the volume of a fiber τ and the surface area of a fiber σ, and is written as

$$V = - \left(\frac{k''\varepsilon^3}{(1-\varepsilon)^2\mu}\right)\left(\frac{\tau}{\sigma}\right)^2\left(\frac{dp}{dx}\right) \qquad (11)$$

Note that τ/σ is an effective fiber diameter, and k" is the inverse of the Kozeny constant k'. Fowler and Hertel verified equation (11) for $0.5 \leq \varepsilon \leq 0.9$ using wool, cotton, rayon, kapok and glass wool fibers.

Generally all early experimental investigations of porous media permeability were conducted at low porosities, i.e., for densely-packed media. The results are therefore not necessarily applicable to highly permeable media such as gels or polymer solutions, which generally have porosities greater than 0.9.

We now examine some theories which were developed for media which are fibrous and loosely-packed, i.e. those in which the strands generally occupy less than 10% of the total volume.

3. FLOW THROUGH 2-D ARRAYS OF CIRCULAR CYLINDERS

3.1 Longitudinal Flow

Around the same time that Kozeny and Carman were developing Poiseuille-type equations to estimate porous media hydrodynamic permeability, Emersleben (1925) solved the problem of low Reynolds number flow parallel to a periodic, infinite, square array of parallel circular cylinders. A representative unit cell, defined by a square enclosing a single cylinder (fiber), constituted the model for the entire array. The boundary conditions were:

a) zero normal and tangential velocities on the cylinder surface, and

b) zero shear stress and constant velocity at the edges of the unit cell, which were located approximately by a series of Epstein-Zeta functions.

These boundary conditions will henceforth be referred to as 'shear-free' boundary conditions. Emersleben solved the Stokes equation and integrated over the cell area to find the following equation for the hydrodynamic permeability,

$$k = \frac{1}{\mu} \left(\frac{a}{2\pi}\right)^2 F(r,\theta), \qquad (12)$$

where $F(r,\theta)$ is a function of Epstein-Zeta functions. Emersleben provided graphs for $F(r,\theta)$, but no comparisons were made between his predictions and experimental data.

Langmuir (1942) also solved the Stokes equations for parallel flow through a periodic array of parallel circular cylinders. He used the shear free boundary conditions for a unit cell and derived the following expression for the superficial velocity,

$$V = \frac{a^2}{\mu}\left(\frac{-\ln\phi + 2\phi - \phi^2/2 - 3/2}{4\phi}\right)\frac{dp}{dx} \quad , \tag{13}$$

where ϕ is the fractional solid volume, i.e., $\phi = 1-\varepsilon$. By comparing equation (13) with equations (3) and (10), it is found that

$$k = a^2\left(\frac{-\ln\phi + 2\phi - \phi^2/2 - 3/2}{4\phi}\right) \tag{14}$$

and

$$k' = \left\{\frac{(1-\phi)^3}{\phi(-\ln\phi + 2\phi - \phi^2/2 - 3/2)}\right\} \tag{15}$$

From equation (15), Langmuir concluded that the Kozeny constant k' is not constant, but a function of the solidity of the medium. The equation shows that, for values of ϕ between 1 and 0.5, which covers the range of most experimental data available at that time, k' varies between 3.00 and 3.67, which is not a large variation. However, for low solidity values of 0.1, 0.01 and 0.001, the corresponding values of k' are 7.24, 31.2 and 184.0. For this type of porous medium, therefore, the Kozeny parameter is definitely not constant for high porosities.

Happel (1959) was another who solved the parallel flow problem for an infinite periodic array of circular cylinders. A representative unit cell was defined by a cylindrical fluid boundary of radius b concentric with a single fiber of

radius a. The radius b was chosen to correspond to the actual solidity, that is, ϕ is defined as

$$\phi = a^2/b^2. \qquad (16)$$

By using a cylindrical instead of a square boundary, Happel was able to greatly simplify the mathematics in solving the Stokes equation. He also used the shear free boundary conditions, and his solution is identical to that of Langmuir (equation 13). He noted that his predictions of the Kozeny constant (equation 15) were higher than Sullivan's (1942) experimentally-determined values for θ in the range of $0.2 \leq \phi \leq 0.45$. However, Sullivan's experiments were conducted on combed textile fibers, and exact agreement would not be expected because the fibres were not all straight, parallel, and of the same diameter.

At about the same time, Sparrow & Loeffler (1959) solved the parallel flow problem for triangular as well as square arrays of parallel circular cylinders. For the square array, the unit cell was a square (like Emersleben) and for the triangular array, the unit cell was a triangle. Shear free boundary conditions were applied. However, instead of using second order Epstein-Zeta functions to define the square or triangular fluid boundaries as Emersleben did, Sparrow & Loeffler employed a power series solution to the Stokes equation. The series generally required no more than 6 terms to obtain the desired accuracy. At high porosities, the predicted permeability did not depend significantly on array arrangement (i.e.,

square versus triangular). For the case of contacting cylinders (minimum porosity), Sparrow & Loeffler found excellent agreement between their theory and Sullivan's (1942) experimental data with aligned drill rods.

Banerjee & Hadaller (1973) also solved the parallel flow problem for a triangular array of parallel circular cylinders using a variational technique. Shear free boundary conditions were again specified. The predicted velocity profiles and effective cylinder friction factors agree well with those calculated by Sparrow & Loeffler.

A comparison of the available theories, i.e. those of Emersleben, Happel and Sparrow & Loeffler, was provided by Happel & Brenner (1965). Using the Kozeny constant as the basis of comparison, they found that the triangular array predictions of Sparrow & Loeffler agree very well with Happel's predictions, particularly at porosities above 0.2. Sparrow & Loeffler's square-array predictions are lower than the triangular-array predictions for porosities below approximately 0.5, but at higher porosities, the two sets of predictions quickly converge. Emersleben's predictions are well below those of Happel and Sparrow & Loeffler for porosities below 0.8. All theories agree at porosities above 0.9 - a most important finding because of the possible application of these theories to polymer solutions, for which the porosity is generally greater than 0.9.

Sparrow & Loeffler's results for the triangular array were confirmed by Banerjee & Hadaller (1973) who used a

variational technique instead of power series to obtain a solution. More recently, Drummond & Tahir (1983) solved the parallel flow problem for square, triangular, hexagonal and rectangular arrays of parallel cylinders using a method of singularities. Shear free boundary conditions were used for each array, and the following estimates of hydrodynamic permeability were found:

a) square array

$$k = (\frac{a^2}{4\phi})(-\ln\phi - 1.476 + 2\phi - \frac{\phi^2}{2} + 0(\phi^4)) \qquad (17)$$

b) triangular array

$$k = (\frac{a^2}{4\phi})(-\ln\phi - 1.498 + 2\phi - \frac{\phi^2}{2} + 0(\phi^6)) \qquad (18)$$

c) hexagonal array

$$k = (\frac{a^2}{4\phi})(-\ln\phi - 1.354 + 2\phi - \frac{\phi^2}{2} - 0.358\phi^3 + 0(\phi^6) \qquad (19)$$

d) rectangular array

$$k = (\frac{a^2}{4\phi})(-\ln\phi - 1.130 + 2\phi - 1.197\phi^2 + 0(\phi^3)) \qquad (20)$$

The similarities of these four among themselves equations and with Happel's equation (14) prompted Drummond & Tahir to propose the general expression

$$k = (\frac{a^2}{4\phi})(-\ln\phi - K' + 2\phi - \phi^2/2) \qquad (21)$$

where K' is an experimentally determined value which reflects the arrangement of the fibers. Drummond & Tahir found a theoretical variation between 1.13 and approximately 1.5 for K', depending on the fiber arrangement, and Happel and Langmuir each predicted a value of 1.5. However, no comparisons of these theories to experimental data have been made.

3.2 Transverse Flow

The first attack on transverse flow past circular cylinders was made by Tamada & Fujikawa (1957), who solved the problem of flow perpendicular to a single infinite row of parallel circular cylinders (the plane of the cylinders is normal to the flow). Oseen's equations for low-Reynolds-number two-dimensional flow around a circular cylinder were used as governing equations. The drag D per unit length of cylinder was calculated to be

$$D = \frac{8\pi\mu U}{1 - \log \beta^2 + \beta^2/6 + O(\beta^4)} \qquad (22)$$

$$\beta = 2\pi a/h, \qquad (23)$$

where a is the cylinder radius and h is the cylinder pitch. No comparisons of equation (22) were made to experimental data.

Happel (1959) analyzed the problem of perpendicular flow to a two-dimensional infinite array of parallel circular cylinders. He used the same unit cell approach as in the parallel flow case, and again applied shear free boundary conditions. His solution for the hydrodynamic permeability is

$$k = \frac{a^2}{8\phi}\left(-\ln\phi + \frac{\phi^2-1}{\phi^2+1}\right), \qquad (24)$$

which was briefly compared with experimental data for fibrous air filters which had solidities greater than 0.2 (Davies (1948, 1952) and Sullivan (1942)). The theoretical predictions were slightly lower than measured permeabilities: this agreement is much better than expected in view of the fact that the fibres were randomly oriented in planes perpendicular to the flow.

Kuwabara (1959) solved the same perpendicular flow problem as Happel, but used a different set of conditions at the edge of the circular cell, i.e., at r = b. While Happel used a condition of zero shear stress there , Kuwabara specified zero vorticity. He solved the Stokes equation for the flow field, integrated over the flow area, and arrived at the following expression for hydrodynamic permeability

$$k = (\frac{a^2}{8\phi})(-\ln\phi - 1.5 + 2\phi). \qquad (26)$$

This equation yields values somewhat below those predicted by Happel. Hence there is a poorer agreement with the experimental data of Davies (1948, 1952) and Sullivan (1942) mentioned earlier, and so the shear free boundary condition seems a better choice over the vorticity free condition. However, velocity profiles measured by Kirsch & Fuchs (1967) show better agreement with Kuwabara's predictions, and consequently the question as to which is the more appropriate boundary condition is still unresolved.

A different technique was advanced by Hasimoto (1959) for the case of a square array of parallel circular cylinders. His method of periodic solutions was similar to Emersleben's, but he used Fourier series instead of the more complex second-order Epstein-Zeta functions. Good agreement was found between this method and earlier work by the same author using elliptic functions. His equations for permeability are:

$$k = (\frac{a^2}{8\phi})(-\ln\phi - 1.476) \ldots \qquad (27)$$

using Fourier series, and

$$k = (\frac{a^2}{8\phi})(-\ln\phi - 1.476 + 2\phi + 0(\phi^2)) \qquad (28)$$

by elliptic functions. The similarity of these equations with equations (26) and (21) should be noted.

The most recent work on square arrays is by Sangani & Acrivos (1982), who also treated the hexagonal array. Using shear free boundary conditions and a method combining numerics and Sparrow & Loeffler's technique, they found a solution which is asymptotic to Hasimoto's theory for relatively low solidities and asymptotic to lubrication theory for high solidities. Their work was aimed at tube banks in heat exchanges but no experimental comparisons have been made to their theory.

Drummond & Tahir (1983) also recently solved the perpendicular flow problem for a square array of parallel circular cylinders. Using the same technique as they did for the parallel flow problem, they determined the hydrodynamic permeability to be

$$k = \left(\frac{a^2}{8\phi}\right)(-\ln\phi - 1.476 + 2\phi - 1.774\phi^2 + 0(\phi^3)) \qquad (29)$$

This equation agrees well with the predictions of Happel, Kuwabara, Hasimoto and Sangani & Acrivos. Note that the general equation (21) suggested by Drummond & Tahir for parallel flow, if halved, is equally applicable to transverse flow. As before, the constant K' varies with fiber arrangement. As in the parallel flow predictions, Drummond & Tahir did not compare their perpendicular flow predictions with experimental data.

4. FLOW THROUGH 3-D NETWORKS

4.1 Cubical Lattice of Circular Cylinders

In their book on low Reynolds number hydrodynamics, Happel & Brenner (1965) combined Happel's (1959) results for flow parallel and perpendicular to rod arrays to predict permeability for a cubical array of rods, i.e. for a three-dimensional lattice. They calculated some values of the Kozeny constant for the cubical array by taking 2/3 of the Kozeny constant for perpendicular flow plus 1/3 of the Kozeny constant for parallel flow. No explicit algebraic formula for permeability was presented, and no comparisons were made with experimental data.

Jackson & James (1982) combined Happel's (1959) results in another way and arrived at a different relation for the hydrodynamic permeability. In their treatment the cubical permeability k is calculated as follows

$$\frac{1}{k(\phi)} = \frac{1}{k_1(\frac{2\phi}{3})} + \frac{1}{k_2(\frac{\phi}{3})} \qquad (30)$$

where k_1 is Happel's permeability for perpendicular flow and k_2 is his permeability for parallel flow. At low solidities, their equation for k reduces to

$$k = \frac{3a^2}{8\phi}(-\ln\phi - 0.56 + 0(\frac{1}{\ln\phi})) \; . \qquad (31)$$

This expression was compared to experimental data for a polymer solution (hyaluronic acid), and agreement was very good for the range of solidities tested, $0.0003 \leq \phi \leq 0.01$.

4.2 Random Array Models

Spielman & Goren (1968) applied a technique by Brinkman (1947) to solve the problem of flow though a random array of fibers. The technique involves solution of a modified Stokes equation, written in the form

$$\nabla p = \mu\nabla^2\bar{V} - \mu k\bar{V} \qquad (32)$$

where k is the porous medium hydrodynamic permeability. For flow well away from a fiber ($r\to\infty$), the Darcy term $\mu k\bar{V}$ dominates as velocity gradients vanish, i.e. $\nabla^2\bar{V}\to 0$. Thus boundary conditions can be applied at $r = \infty$ without encountering the Stokes paradox. Close to the fiber, the conventional $\mu\nabla^2\bar{V}$ viscous term dominates the Darcy term, and equation (32) approaches the Stokes equation. Thus by introducing the $\mu k\bar{V}$ Darcy term, Spielman & Goren were able to solve the flow problem by effectively accounting for local effects ($\mu\nabla^2\bar{V}$) as well as the regional influence of the rest of the porous medium ($\mu k\bar{V}$). Because equation (32) can be solved using boundary conditions applied at $r = \infty$, the solution avoids the complex mathematical techniques required to describe the triangular, square, hexagonal or rectangular boundaries of the unit cell models described in section 3. Speilman & Goren developed separate equations for the following four types of random arrangement of fibers by choosing appropriate boundary conditions;

a) fibers lying in planes perpendicular to the direction of flow, but having completely random angles in those planes (application: paper and some types of fabric filters),

(b) fibers parallel to the direction of flow (application: some types of fabric filters and heat exchangers),

(c) fibers lying in planes parallel to the direction of flow, but having completely random angles in those planes. (application: paper and some types of fabric filters),

(d) fibers in completely random orientations (application: polymer solutions, gels, and randomly packed beds of fibers),

Unfortunately the derived expressions for k are not explicit and involve Bessel functions. However, Spielman & Goren made a relative comparison of the four cases described above by plotting the predictions in terms of a dimensionless pressure gradient versus solidity. As might be expected, case (a) provides the highest resistance, followed by cases (d), (c) and then (b). They also graphically compared case (a) with the theories of Happel, Kuwabara, and an experimental correlation of Davies' (1952). This correlation, which was based on filter pad data over a range of solidities between 0.006 and 0.3, has the form

$$k = \frac{a^2}{16\phi^{1.5}(1 + 56\phi^3)} \qquad (33)$$

Both Happel's and Spielman & Goren's theories agree reasonably well with Davies correlation at solidities greater than 0.02. Below this solidity the theories and Davies' correlation diverge, with the theories underpredicting the permeability.

Kuwabara's theory consistently underpredicts permeability over the entire range of solidities by about 40%.

Yu & Soong (1975) recognized that in a real porous medium the variation in porosity may have a significant effect. They modelled this variation by assuming that flow paths are actually a distribution of parallel paths, each with a different porosity. They pointed out that the medium porosity is actually the mean porosity of a distribution of porosities. Since hydraulic resistance is not a linear function of porosity, the weighted medium permeability is not the same as the permeability based on a simple average porosity. An analysis in this vein led them to develop a 'random cell' model which in effect is a means of randomizing the permeability for a given type of structure. When their randomization technique is applied to Kuwabara's model, the permeability is 50% higher than that predicted by equation (26). The revised estimates of permeability agree well with Davies' correlation and with the data of Billings (1966) for solidities greater than .04 but are too high at lower solidities. When the random cell is applied to Happel's model, the higher permeabilities agree well with the data of Baumstarke et al (1959).

5. CLOSURE

5.1 Conclusions

Early efforts to predict pressure drop versus flow rate in a fibrous porous medium were based on Poiseuille flow analogies and led to the practice of characterizing a medium by its Kozeny constant.

Later theories, based on solution of the Stokes equation, resulted in a variety of expressions for the medium's hydrodynamic permeability. In the latest available work, Drummond & Tahir suggest the following two expressions for flow parallel with, and normal to, arrays of parallel fibers:

$$\text{(a)}\quad k_p = \frac{a^2}{4\phi}\left(-\ln\phi - K_p' + 2\phi - \frac{\phi^2}{2}\right) \tag{34}$$

$$\text{(b)}\quad k_n = \frac{a^2}{8\phi}\left(-\ln\phi - K_n' + 2\phi - \frac{\phi^2}{2}\right) \tag{35}$$

These equations, and similar ones from other theoretical studies, show that the Kozeny constant used in the Poiseuille analogy theories is constant only for high solidities.

The only theoretical equation for an array of fibers arranged in a cubical fashion has been provided by Jackson & James. Good agreement with experimental data on low concentration polymer solutions was found.

Spielman & Goren have provided implicit expressions for permeability for various random arrays of fibers using a method first employed by Brinkman. Their theory, however, does not agree well with the low porosity data of Davies.

Yu & Soong introduced statistical methods to treat the inhomogeneity of porous media. They have shown that an inhomogeneous medium always has a higher permeability than a homogeneous one. This interesting concept shows promise in applying various homogeneous theories to real heterogeneous media.

In preparing this review, it became quite apparent that there is no recent comprehensive comparison of all the theoretical predictions of hydrodynamic permeability for fibrous porous media. A straightforward tabulation and/or graphical comparison would be of considerable use. Likewise, there is no recent comprehensive review of experimental data in relation to these theories. Such a review would aid in assessing which theory shows the most potential in modelling various types of fibrous porous media over a large range of porosities and which might be the most useful for modelling entangled polymer skeins in solution.

5.2 Directions for Future Research

The suggestions made in the previous section, viz., comprehensive comparisons between theories and between theories and experiments, follow naturally from the review and would be of interest to a large technical community. However, other studies are likely to be of more direct value to those interested in hydrodynamic forces on macromolecules. For this application, a two-pronged attack is suggested:

1. Theoretical modelling. The presently available theories are for media formed by long straight rods, a shape

which is far from the random-coil configuration of a long-chain molecule in solution. An analytical study is required to address the influences of curvature, random orientation and segment density on flow resistance through a coil or through entangled coils. The ultimate goal at such an analysis would be to estimate the permeability k of a single macromolecule or a solution of macromolecules, given the chain diameter and the solid volume fraction of the chain or chains.

2. Filtration Experiments. There are very few data on the permeability of polymer chains in chain. Measures of permeability would not only complement the analytical study of (1) but would also be of direct value in applications involving polymers as additives. For example, permeability data for polymers used in enhanced oil recovery would enable engineers to make better estimates of the resistance caused by polymers absorbed on the rock surface or by polymers blocking pores. It is proposed, therefore, to measure the permeability of solutions of selected polymers, namely those employed in the oil and cool industries. Initial tests would deal with nonionic polymers and be designed to assess the influence of polymer type, molecular weight and concentration. Later tests could then be dedicated to the more difficult ionic polymers, for which charge distributions along the chain and in the solvent are also factors.

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SURVEY OF HYDRODYNAMIC EFFECTS WITH MACROMOLECULES

B. DYNAMICS OF LONG CHAIN POLYMERS IN FLOWING SOLVENTS

by

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1. INTRODUCTION

The deformation of a randomly-coiled macromolecule in a flowing solvent is governed by forces due to viscous drag and Brownian motion. This deformation determines continuum variables like stress and birefringence, and thus knowledge of the deformation is essential for characterizing the behaviour of a polymer solution. But, while the physics is straightforward to describe, the mathematics is formidable and consequently various dynamical models have been devised. Chief among these are the well known bead-spring models developed by Rouse and Zimm in the 1950's. Because these models are not accurate in steady flows, various modifications have been made and consequently a number of theoretical models is now available. The purpose of the present work is to review the models and to critically assess them by comparing their predictions with experimental data.

The models attempt to describe the rheological behaviour of dilute solutions. In order to provide a proper context for comparisons with experimental results, the first part of this survey covers experimental rheology. In reviewing experimental work, the emphasis is on solutions which are dilute (no molecular overlap), or at most semi-dilute, and on aqueous systems. These criteria reflect conditions in the practical situations where polymers are used for hydrodynamic effect: the solvent is invariably water and the solute concentration is small. The particular polymers of interest to the energy industry, and

therefore the ones covered in this survey, are polyacrylamides, polyethylene oxide and polysaccharides. The survey focusses on the behaviour of these polymers in shear and extensional flow. There is abundant literature on all polymers in oscillatory shear flow, but this flow will be treated only briefly because shear and extension are the components of any practical flow.

It is assumed here that the reader is familiar with the basic variables of non-Newtonian rheology, and so terms like intrinsic viscosity, extensional viscosity and first normal stress difference will not be defined. If unfamiliar, these and other terms can be found in standard texts on rheology.

While this survey is presented as a background for later assessment of the models, it also serves as an adjunct for the companion review on flow through porous media. That is, to understand non-Newtonian flow in porous materials, it is useful to know the rheological properties of the fluids. Porous medium flow is a combination of shear plus extension and, while these fluids are routinely characterized in shear, it is exceedingly difficult to characterize them in extension. Delineating the current state of knowledge in shear and extension should be useful, then, for the EMR porous media review as well.

After covering shear and extensional flow data for aqueous polymer systems, the molecular models are reviewed, starting with the classical Rouse theory for a random coil. The various modifications to this model – viz., hydrodynamic interaction, internal viscosity, and nonlinear springs – are dealt with in turn. Sometimes the full multi-bead chain is treated and sometimes the analysis is limited to the mathematically simpler

dumbbell model. Because the rheology of a suspension of particles is similar to that of a polymer solution, the survey includes the portion of suspension theory which is relevant, namely, that dealing with long or elongated particles. The survey also discusses the porous sphere model. This model is not usually included in reviews of molecular models, but it is hydrodynamically sound and provides a useful alternate approach.

There are 112 references in the Bibliography of this review, these being the most important of the 300 papers collected in the literature search. The search was intended to be comprehensive, but not necessarily exhaustive, and it is unlikely that a major paper was missed. The idea was not to explore every nook and cranny, but rather to grasp the whole of the field and assess the contributions to it.

Dilute Solutions

Since this report emphasizes dilute solutions, it is essential to define the term. 'Dilute' strictly means that there are no interactions between molecules and hence concentration effects are linear. For polymers used in energy applications, a dilute solution has a polymer concentration less than 500 parts per million (ppm) when the solvent is stationary, and several times less when the solvent is flowing because of hydrodynamic interactions. The term 'semi-dilute' indicates the bordering regime where inter molecular entanglements dominate the rheology. Confusion sometimes arises because authors use the term loosely and because the role of hydrodynamic interaction is not understood.

2. EXPERIMENTAL RHEOLOGY OF DILUTE SOLUTIONS

2.1 Shear Flow

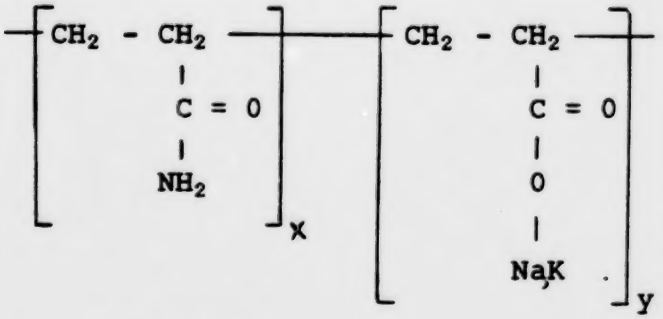
The rheological property most commonly measured is viscosity. For Newtonian fluids, measurement is simple because viscosity is independent of shear rate both in steady and oscillatory shear. However, the viscosity is rarely constant when the fluid is a dilute solution or suspension, and consequently a proper measurement of viscosity for a non-Newtonian fluid is over a full range of shear rates. Since these fluids usually have near-constant viscosities at very low rates of shear (generally $<10^{-3}$ s^{-1}) and at very high rates of shear ($>10^{2}$ s^{-1}), a proper measurement of viscosity requires data over six decades of shear rate.

In the field of polymer chemistry, it is common make viscosity measurements in oscillatory shear and not in steady shear. However, data from the two flows do not usually coincide, primarily because molecular deformation is small in the former and large in the latter. Because steady shear is more related to practical flows, as mentioned in the Introduction, viscometric steady shear data will dominate in this report.

2.1.1 Polyacrylamide Solutions

The most widely used polymer in energy-related applications is polyacrylamide. This polymer is important because it does

not degrade easily. Yet its most important characteristic is that it is generally partly hydrolyzed and hence is a polyelectrolyte. The chain is made up of different proportions of acrylamide and acrylic acid, as the following chemical structure shows (Muller et al, 1979).



Degree of Hydrolysis

$$\alpha = \frac{y}{x + y}$$

The y groups are negatively charged, and, if there are no positive ions in the solvent to neutralize them, the charges repel each other and cause the molecular coil to expand. If, however, positive ions are present, some or all of the charges will be neutralized or shielded, and the coil will be correspondingly smaller. Since hydrodynamic effects by polymers depend markedly on coil size, then the number and type of ions in the solvent must be known, as well as the chain length (molecular weight) and degree of hydrolysis of the solute. The main hydrodynamic property of interest is viscosity, of course, but coil size also affects the sedimentation coefficient which is an important property in applications like flocculation.

Because of partial hydrolysis and because of industrial methods of production, polyacrylamides are difficult to characterize. They are sold under various trade names, and are

designated as nonionic (neutral), anionic or cationic. The first two are the most common by far and thus are the ones of interest in this review. The first category, however, may be only an ideal. D.L. Hunston (private communication) and co-workers at the U.S. Naval Research Laboratory tested about 15 commercial samples of polyacrylamide, some of which were labelled 'nonionic' by the manufacturer, and all proved to be partially hydrolyzed. This judgement was based on anomalies in measurements of intrinsic viscosity, which is very sensitive to coil size. One should therefore treat all polyacrylamides as anionic and add known amounts of salt to the solvent to have stable solutions. Otherwise the coil is highly sensitive to trace ions in the solvent and it then becomes very difficult to reproduce solution properties.

Another fact of life with polyacrylamides is that industrial products contain substances in addition to the polymer. Francois et al (1979) reported that their sample of CALGON contained 17.5% salt impurities and Durst et al (1981) found 12% to 18% water in four industrial samples. Hence, experimenters using as-received industrial polyacrylamides cannot expect to duplicate work from other laboratories and will even have difficulty correlating their own results with different samples. Yet, for the researcher who wants to relate his work to end-use application, use of commercial products is a necessity. The problem is usually got around by adding a large amount of salt to the solvent, more than is necessary to shield the charges along the chain. The most commonly used salt is NaCℓ, and the

amount is of order 0.5 M. In the next two sections, the influence of ion concentration on polymer hydrodynamics will be seen through two properties, the solution viscosity and the solute intrinsic viscosity.

Viscosity

The viscosity of a polyacrylamide solution depends on the properties of solute and solvent and on the shear rate. The influence of salts is well demonstrated by the work of Muller et al (1979) and Mungan (1972). The first group showed that the viscosity of a dilute solution varies significantly with concentration of potassium hydroxide, sodium chloride, calcium chloride or magnesium chloride. For the last three salts, the viscosity rises dramatically as the salt concentration approaches zero, indicating considerable expansion of the molecular coils. With NaCℓ, for example, the viscosity rises ten times as the concentration decreases from 0.1 M to zero, at 'zero' shear rate. Similar results with NaCℓ were reported earlier by Mungan (1972), who also showed that the divalent cations, magnesium and calcium, had a more pronounced effect than the univalent sodium. Ward & Martin (1981) have carried this line of research one step further by mixing both types of ions in known proportions. Since polyacrylamides are used in oilfields which typically contain brines of various ions, they made a systematic study of viscosity in brines of more than one type of cation.

Equally important to oil recovery (and other flows) is the variation of viscosity with shear rate. The most extensive data of this sort are by Mungan (1972) and Friebe (1976). Both measured viscosity over seven decades of shear rate and for concentrations from semi-dilute to extremely dilute. Friebe, in fact, reports data for concentration as low as 2.5 ppm. The main difference between the two works lies in the solvents: as mentioned earlier, Mungan's solvents were brines of various ionic concentration, while Friebe used water-glycerol mixtures in various proportions. Whatever the solvent, all the data look similar, and a typical example is shown on the next page. The figure shows that polyacrylamide solutions are highly non-Newtonian, even in the very dilute regime. The molecular mechanics underlying this behaviour are not fully understood and molecular models have only partially succeeded in simulating experimental results. This behaviour will be discussed further in the section on molecular modelling, but for the moment two points must be made: the strong variation in viscosity must be taken into account in applications, and a single-point measurement of viscosity of a solution is not meaningful unless the shear rate is also specified.

While the viscosity measurements of Mungan and Friebe are the the most comprehensive to date, other data are also available and are included here for completeness. Michele (1977) reports viscosities of dilute and semi-dilute solutions of Separan AP30 over seven decades of shear rate (Separan is Dow Chemical's trade name for polyacrylamide). Acierno et al (1974)

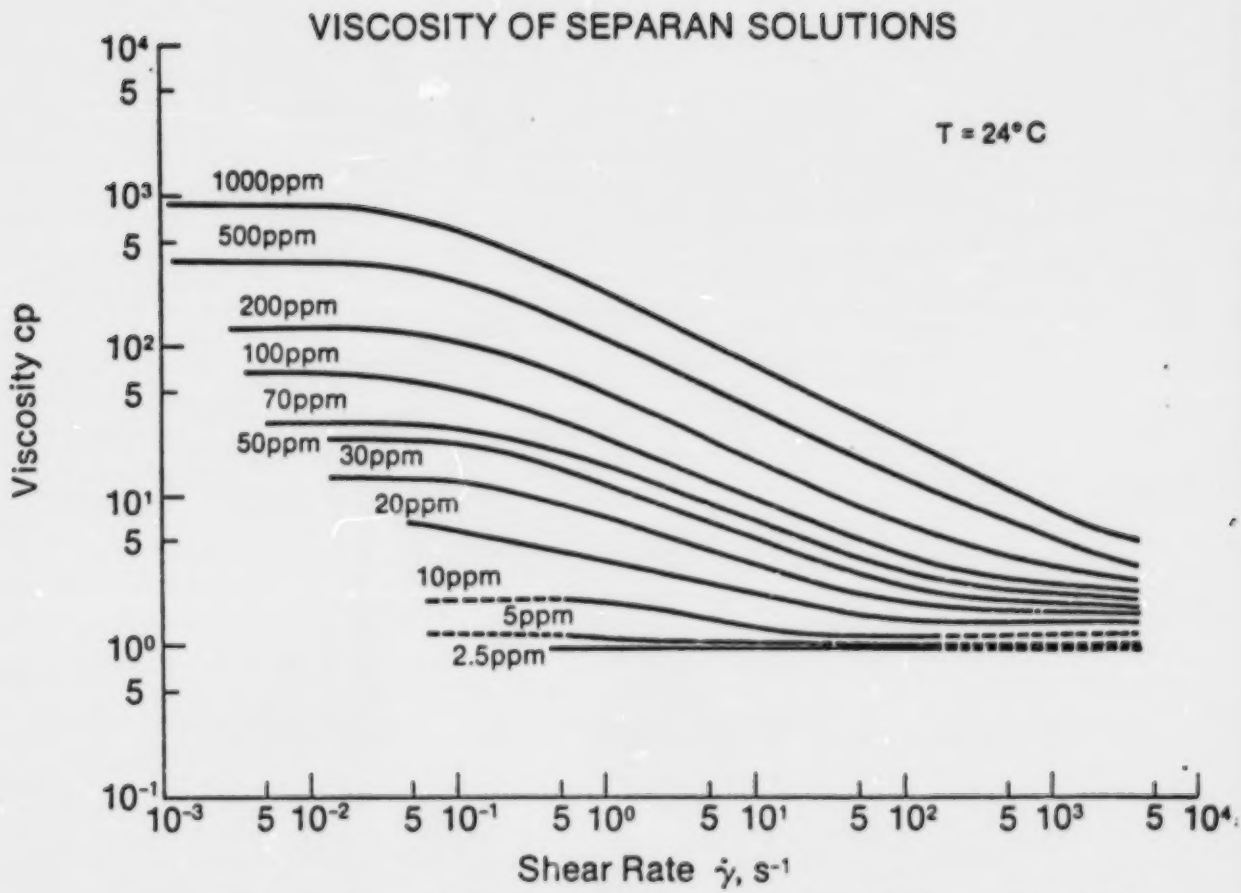


Fig 10; from H.W. Friebe, Rheol. Acta, Vol 15, pg 340 (1976)

measured the viscosity of similar concentrations of Separan NP20, but over a much narrower range of shear rates. Muller et al (1979) found the effect of monovalent and divalent salts on coil expansion by viscosity and light-scattering measurements. The latter measurements yielded the mean radius of gyration of molecules, and so their data usefully relate coil size to ionic concentration. Lange & Rehage (1980) and Jones (1979) also report viscosity measurements of polyacrylamide solutions; some of the latter's data show the anomalous behaviour in viscosity when there are an insufficient number of ions to shield the charges.

Two other works on the non-Newtonian behaviour of polyacrylamide solutions should be mentioned. Argumedo et al (1978) measured the rheological properties of Separan AP-273 in a Weissenberg rheogoniometer, for concentrations from 0.012% to 2.0%. Measurements of shear viscosity, dynamic (oscillatory) viscosity, first normal stress difference, and storage modulus were well fitted by a particular rheological model, the four-parameter Carreau model B (see page 445 of Bird, Armstrong & Hassager). Because their minimum concentration, 120 ppm, is nominally in the dilute regime, the close fit leads them to claim that the model can be applied to more dilute solutions by extrapolating the parameters. This is doubtful, because even at 120 ppm, the molecules were likely highly expanded and therefore entangled in their salt-free solutions. In the strictly dilute regime where entanglements do not contribute to the mechanics, even the form of the constitutive relations is likely to be

different. Hence their successful rheological model will probably not correlate data in the truly dilute regime.

The other work of interest is by Darby (1970). He measured the steady shear viscosity of dilute polyacrylamide solutions over seven decades in shear rate, and, more importantly, devised a clever way of determining fluid relaxation times from a specially-designed transient response apparatus. Since his transient data were well fitted by an Oldroyd model (see Bird, Armstrong & Hassager), he was able to determine both the retardation and relaxation times of the solutions. These times were of order 0.1 s and 1 s respectively, for solutions of 250 and 500 ppm solute. These times are much higher than expected for dilute solutions (Rouse relaxation times, for example, are generally of order 10^{-2} to 10^{-3} s for dilute solutions), and because the solvent was salt-free 'distilled water', his unusually long times are probably due to entanglements.

These last papers re-emphasize the importance of known ionic strength for solutions of partially hydrolyzed polyacrylamides. With uncontrolled amounts of a cation present, it is exceedingly difficult to know how small the polymer concentration must be to create a truly dilute solution. It is important to create dilute solutions in order to use the well-established theoretical and empirical equations which relate mean molecular weight, intrinsic viscosity and the sedimentation coefficient. In the next section, we shall see that these equations have been determined for polyacrylamide solutions, often with salt in the solvent to ensure diluteness.

Intrinsic Viscosity

For rheological purposes, the single most important characteristic of a polymer solution is the intrinsic viscosity of the solute. This property is a measure of the hydrodynamic influence of a single molecule and therefore depends on the length of the molecule and on the type and temperature of the solvent. In fact these latter conditions must accompany any statement about the intrinsic viscosity of a polymer sample.

A thorough characterization of polyacrylamides, including measurements of intrinsic viscosity, has been carried out by Klein and co-workers (1978a, 1978b, 1980). Of principal interest to us are his relations between the intrinsic viscosity $[\eta]$ and mean molecular weight $\bar{M}_w$. The $[\eta]$-$\bar{M}_w$ relation always has the form

$$[\eta] = K\bar{M}_w^a ,$$

and Klein et al found K and a for nonionic polyacrylamide in three solvents: distilled water, ethylene glycol, and 0.5 M aqueous NaCℓ solution, all at 298 K. Klein and company made their own polyacrylamides, and hence were able to produce truly nonionic samples. In their synthesis, they controlled both molecular weight and degree of hydrolysis and consequently found changes in K and a as the acrylamide fraction varied from 30 to 100 mol-% (the solvent was 0.5 M aqueous NaCℓ at 298 K). It should be noted that molecular weights were determined by light scattering, and that viscosities were measured in the extremely low shear rate range where viscosity is independent of shear rate.

Other work has helped to characterize the polymer. Francois et al (1979) measured $[\eta]$, $\bar{M}_w$ and the radius of gyration of nonionic polyacrylamide samples in 0.1 M aqueous NaCℓ solutions. Munk et al (1980) measured the sedimentation coefficient s_0 and intrinsic viscosity of six unhydrolyzed polyacrylamide samples; by using established correlations of s_0 and $\bar{M}_w$, they were able to determine $[\eta]$-$\bar{M}_w$ relations when the solvent was water, 0.2 M and 1.0 M NaCℓ. While their constants K and a are different from those of Klein et al, the curves are similar on log-log plots of $[\eta]$ vs. $\bar{M}_w$. The paper of Munk et al also provides useful hints on the preparation of polyacrylamide solutions. One defect of their work is that the shear rate is not clearly identified, and in that regard Shawki & Hamielec (1979) have provided a needed service by relating measurements of $[\eta]$ at low shear rate to those at high shear rate where the viscosity is again Newtonian. Hence they present $[\eta]$-$\bar{M}_w$ relations where $[\eta]$ is determined at high shear rates.

Other useful information on polyacrylamide solutions has been furnished by Narkis & Rebhun (1966) on aging, by Shyluk & Stowe (1969) on aging and disaggregation, by Quayle (1967) on agglomerates, and by Abdel-Alin & Hamielec (1973) on shear degradation.

2.1.2 Polyethylene Oxide Solutions

Polyethylene oxide is a neutral polymer with a particularly simple structure, $\{CH_2\text{-}O\}_n$, and in aqueous solution, it has

found many applications. In contrast to the behaviour of polyacrylamide solutions, the shear rheology of dilute aqueous solutions of polyethylene oxide is simple: they are Newtonian in steady shear. Viscometric data by Caraher (1965) in the shear rate range 10^{-1} to 10 s^{-1}, by Belokon et al (1973) in the range 10^{0} to 10^{3} s^{-1}, and by Hoyt & Fabula (1964) in the range 10^{3} to 10^{6} s^{-1} all show that the viscosity of a dilute polyethylene oxide (PEO) solution is independent of shear rate. It is not clear why data for this polymer are Newtonian, because nonionic polyacrylamide is also a neutral polymer, and 50 ppm of that polymer produces ten-fold variations in viscosity over the same range of shear rates (see figure on page 9). One has to conclude that mechanics of the two polymers are quite different in a shear flow, that is, the two molecules deform and rotate in dissimilar ways.

The only data contrary to the above picture are those of Layec-Raphalen & Wolff (1980). Their paper is difficult to read, but their results seem to indicate that the intrinsic viscosity of a PEO sample decreases with shear rate. Details of their solutions and their technique are so sketchy that the results cannot be given much weight.

The above were data all obtained in tube flow, and there is no reason to suspect that the behaviour would be different in Couette flow. Some anomalies, however, have been reported for PEO solutions in small tubes. Ouibrahim (1978) suggests that the apparent viscosity depends on tube diameter, but his most dilute solution which shows this behaviour is 300 ppm, and thus

his data can be explained by intermolecular entanglement. Kalashnikov & Vlasov (1978) also report a tube diameter effect with PEO solutions. But, while Ouibrahim's results show anomalous behaviour when tube diameters decrease to 30 μm, Kalashnikov & Vlasov's data show anomalous behaviour for tube diameters greater than 2 mm. Their data strongly suggest that non-Newtonian effects occurred at the tube entrances, although the pattern of their data is not consistent with the entrance effects well characterized by Moan et al (1979) and Chauveteau & Moan (1981). Rather, Kalashnikov & Vlasov (1978) suggest that aggregates are responsible, but it is difficult to imagine an aggregate scale of 2 mm in their 50 ppm solution.

Overall, it would appear that dilute PEO solutions are Newtonian in shear. No one has investigated the rheology properly using a Couette flow apparatus, but the available data suggest that such an investigation is not worth the effort.

2.1.3 Polysaccharide Solutions

A polymer group which is becoming increasingly important for hydrodynamic application is the polysaccharides. Because these polymers are made by bacteria, a proper specification of a polysaccharide is by the bacterium that produced it. For example the polysaccharide of greatest interest is the one produced by the microorganism Xanthomonas campestris; it is variously referred to as xanthan, Xanthan or xanthan gum. Each bacterium produces polymer with a different chemical structure;

consequently the different polysaccharides have different configurations in solution. The chains are negatively charged to some degree, and hence molecular configuration also depends on ions in solution. The shape of the molecule is usually a function of temperature; it is a semi-rigid helix at room temperature but can change to a random flexible coil as the temperature increases (Jones, 1979). All of these factors affect the hydrodynamics and so there is considerable variety in rheological behaviour among the polysaccharides. It is not surprising, then, that the rheological characterization of polysaccharides is not complete.

In a review article on 'gum' solutions, Elliott (1977) describes the viscometric behaviour of these fluids like any other polymer solution: generally shear-thinning, with Newtonian viscosities at very low and very high shear rates. The picture becomes a little more complicated, however, when one looks at the data of Pasika (1977). His plots of reduced viscosity versus concentration show pronounced peaks instead of the usual linear dependence, but he goes on to show that the usual linearity is achieved when there is sufficient salt in the solvent. Like other polyelectrolytes, therefore, statements about intrinsic viscosity of a polysaccharide must also identify the ionic strength of the solvent.

This procedure was followed by Smidsrod & Haug (1971), who measured the intrinsic viscosity of alginate samples with known molecular weights. For an ionic strength of 0.1 M NaCℓ, they found that a in the Mark-Houwink equation, $[\eta] = K\bar{M}_w^a$, was 1.0.

This value signifies that the molecules were not flexible coils but closer to rigid rods. This point was not picked up by them but was the subject of later work by Rinaudo & Milas (1978). By matching intrinsic viscosity data with theoretical results for long rigid particles, they deduced the equivalent axial ratios (or length-to-diameter ratios) of their Xanthan molecules. The values are around 300, which are compatible with the known molecular weights of the samples, but which are an order of magnitude larger than ratios deduced from sedimentation data. Obviously the hydrodynamics for one of these flows has been treated incorrectly. The suspect is sedimentation, because the only available theory treats the molecules as solid rods (Daune, 1962) and not as porous rods. The flow around and through a porous cylinder of finite length has yet to be solved.

The direction of some recent theoretical work follows this vein. Yamakawa and co-workers (1973, 1981) have modelled biological polymers as 'wormlike chains' – helical coils with some degree of flexibility along the axis – and have investigated chain dynamics and diffusion. The hydrodynamics has not been worked out satisfactorily and the current emphasis of the work appears to be on chain configuration. The polymer of primary interest in their work is DNA, but the results should apply equally to polysaccharides once the hydrodynamics are treated properly.

Fundamental research on the non-Newtonian behaviour of polysaccharides, particularly as it relates to enhanced oil recovery, has been carried out by Chauveteau and his colleagues

at the Institut Francais du Pétrole. In a recent paper, Chauveteau (1982) investigated the shear behaviour of xanthan solutions over large variations in shear rate and concentration; it is a comprehensive rheological investigation and likely to become a standard for this polymer. From the viscometric data, Chauveteau was able to deduce molecular overlapping and molecular dimensions of his samples. The article also contains experiments on flow through pores and porous media, and the results will be described in the companion review on porous media flow.

2.1.4 Other Polymers

To help put in perspective the large difference in viscometric behaviour between solutions of polyacrylamide and polyethylene oxide, it may be useful to briefly review the behaviour of some other polymer-solvent combinations.

Moan & Wolff (1973) found that aqueous solutions of carboxymethyl cellulose were shear thinning and that their behaviour in shear flow was equivalent to a suspension of rigid rods. A similar behaviour was found by Sharma (1979) for aqueous solutions of hydroxypropylmethyl cellulose and by Fox et al (1951) for solutions of polyisobutylene in various organic solvent. Other polymers in organic solvents were investigated by Christiansen & Bird (1978) and the behaviour was shear-thinning in every case. A peculiar pattern of shear-thinning at low shear rates and shear-thickening at high rates was found by

Layec-Raphalen & Wolff (1976) for dilute solutions of polystyrene in decalin.

In a long study, Peterlin and co-workers (1965, 1966a, 1966b, 1968) describe time-dependent effects in shear flows with solutions of polymethyl methacrylate in oil. However, their solutions were obviously not strictly dilute, and therefore much of the anomalous behaviour can be ascribed to molecular aggregation and disentanglement.

A good review of non-Newtonian rheology, principally for dilute but also for concentrated solutions, was prepared by Peterlin (1968). The essential fact from that review, and from the papers described above, is that dilute solutions are generally non-Newtonian in shear, the viscosity declining with shear rate but with Newtonian plateaus at very low and very high rates of shear. Hence the Newtonian behaviour of PEO solutions at all shear rates is an oddity in polymer solution rheology.

2.2 Extensional Flow

Non-Newtonian behaviour of dilute polymer solutions is most pronounced in extensional flow. While the viscosity, or resistance to shear, of a solution may change even ten-fold, resistance to extension of the same fluid may increase by factors of order 10^3. This strong non-Newtonian behaviour in extension seems to apply whether or not the solutions are non-Newtonian in shear. Some of the largest extensional effects, for instance, have been reported for PEO solutions which, as just reported, are Newtonian in shear.

In surveying the literature on extensional flow, it seems that the various flow fields which produce extensional motion can be divided into three categories: (i) stretching of a liquid filament in a gaseous environment, (ii) converging flow, as in a channel or at a tube entrance, and (iii) flow in the centre of a four-roller device. This review will group papers according to these categories, and only experimental work will be covered here, for the corresponding theoretical models are discussed in chapter 3.

Assessment of non-Newtonian behaviour in extensional flow is generally made by measuring stress in the straining direction. More precisely, the stress of interest is the additional normal stress due to the dissolved molecules. This stress is often given as a function of strain rate in extension, analogous to tangential stress as a function of strain rate in shear. An equivalent means of expressing extensional resistance is through the property 'extensional viscosity'. In simple terms, this property is the normal stress divided by the rate of extension, analogous to the definition of shear viscosity. However, a strict definition of extensional viscosity involves all three normal stresses, as may be found in standard texts like Schowalter (1977).

A common method of creating extensional flow is by stretching a filament of the liquid. Such free-stream flows can be created by extending a liquid thread (fibre spinning), allowing a stream to fall under gravity, or pulling liquid up and into an elevated tube entrance ('tubeless siphon'). In stretching a

filament, the flow is unquestionably free of shear and is therefore one of pure strain. The strain rate is found by measuring the flow rate and the longitudinal change of filament diameter, usually photographically. The disadvantages are: (i) the initial conditions of the flow are generally not known, (ii) strain rates are not constant along the stream, and (iii) the method is difficult with strictly dilute solutions.

Acierno et al (1974) used both spinning and tubeless siphon experiments to find the elongational viscosity of Separan solutions in glycerol, and Peng & Landel (1976) used the latter method for an unspecified 'anti-mist' additive in jet fuel. Both groups measured extensional viscosities which were 10^3 times the shear viscosity, but it must be noted that their solutions were not dilute, although they claim otherwise. There is less doubt that the solutions tested by Baid & Metzner (1977) and Usui & Sano (1981) were strictly dilute. In a fibre spinning apparatus, the former group tested 100 to 300 ppm solutions of polyacrylamide and found that the normal stress increased with the rate of stretching, to as much as 10^3 times the stress for a purely viscous liquid. The latter group measured extensional viscosity from observations of a falling stream and found exceptionally high viscosity ratios (the ratio of extensional to shear viscosity) for dilute solutions of PEO. Indeed, for a 100 ppm solution of a moderately high molecular weight sample ($M_w = 3.3 \times 10^6$), they found viscosity ratios as high as 27,000 by their technique. This number seems too high for a dilute solution, but other experiments with PEO solutions indicate

that very strong non-Newtonian behaviour is possible when the fluid has a long period of stretching.

Perhaps the most common flow for the study of extensional motion is the flow in a converging channel or at the entrance to a constriction. Visual studies of orifice flow or tube entry flow show that there is a large vortex ring surrounding the opening when polymer is present, in contrast to the simple converging motion with a Newtonian fluid. The toroid guides the central flow toward the constriction and, because of its size, creates a lengthy central flow in which there is ample time for fluid stretching. Hence additional stresses are expected, and these are usually monitored by measuring the extra pressure required to push fluid through the constriction. The main defect of this flow is that the boundary of the central flow is not well defined and investigators are forced to estimate strain rates. Metzner & Metzner (1970) did just that in their landmark paper on orifice flow; from visual studies, they estimated upper and lower bounds for the rate of extension and showed that the viscosity ratio of a 100 ppm Separan solution was at least 500. This result is important because it was the first report of high extensional viscosity for a dilute solution. Interestingly, however, they found no extensional effects for 50 and 25 ppm solutions of the same polymer.

Moan et al (1979) and Chauveteau & Moan (1981) examined entrance flow, initially from the viewpoint of eliminating entrance effects when capillary tubes are used for viscosity measurement. Their work on barely dilute polyacrylamide

solutions indicates that the additional driving pressure is proportional to polymer concentration and roughly to the square of the strain rate. However, in a similar entrance flow, Ouibrahim & Fruman (1980) found that the strain rate dependence was nearly linear. The difference may be explained by the fact that the solutions of Ouibrahim & Fruman were more dilute.

To study how much molecules extend in an elongational flow, Smith et al (1975) focussed a light scattering device on fluid entering a small tube from a large chamber. Their data, reported by Armstrong et al (1980), show that molecules of polyisobutylene in decalin stretched to a length up to four times their rest size. This ratio is what one might expect in such a quickly converging flow, and leads one to question whether additional normal stresses were generated at such low extensions. Unfortunately, the light scattering was not accompanied by hydrodynamic measurements. One other flow of a similar nature and worth noting is the vortex flow of Chiou & Gordon (1980). Here rotational motion was superposed on an entrance flow, and non-Newtonian effects were in evidence for concentrations as low as 3 ppm of PEO. Their conclusion is that extensional flow effects are augmented by shearing in the vortex, a finding which is quite consistent with recent experimental work in our own laboratory on pre-sheared converging flows.

As mentioned before, the basic defect of entrance flow experiments is that the flow field is ill-defined. This situation is improved when the flow is confined to a converging

channel, but only when the Reynolds number is large enough that the core of the flow is free of shear and thus subjected to pure extension. James & Saringer (1980) studied dilute PEO solutions in channels of various shape and found viscosity ratios of order 200. These are significantly below values for unconfined converging flows, but are consistent with the much shorter stretch periods in conical flow. Ou (1981) also carried out experiments in conical channels, but with polyacrylamide as well as polyethylene oxide solutions. Like Ouibrahim & Fruman, he found that the additional driving pressure was proportional to concentration and to the strain rate, and the viscosity ratio was same order as that of James & Saringer. However, his data with polyacrylamide solutions are difficult to interpret, for vortex motion accompanied some of the flows, and the amount of salt in solution affected even the qualitative nature of the results.

Another flow region where extensional motion occurs is at the centre of a 4-roller device. The rollers, arranged at the corners of a square, rotate at the same speed but in counter-rotating directions such that fluid at the centre is subjected to pure strain. It is not possible to measure stresses in this flow, but, because the extensional motion at the centre is virtually stationary, it is an ideal flow to study extension by birefringence. Pope & Keller (1977) and Dandridge et al (1979) investigated dilute and semi-dilute solutions of PEO by birefringence. The former group found that PEO molecules extend more than comparable polystyrene molecules, and the latter group concluded that the PEO molecules are more rigid at concentrations below 150 ppm. In a related experimental set-up with two

rollers (Cressely et al, 1978, 1979), birefringence revealed considerable extension of PEO molecules in concentrated solution whether the rollers rotated in the same or opposite direction.

The most comprehensive study of extensional motion by birefringence methods was by Fuller and Leal (1980a, 1980b). They first mapped the velocity field in a four-roller apparatus to relate velocity gradients at the centre to the known roller speeds. The roller speeds and directions were arranged to generate any two-dimensional flow, from pure rotation to pure strain. They measured the birefringence of dilute solutions of polystyrene in a viscous solvent, and were able to correlate data for a variety of two-dimensional flows. At high strain rates, the birefringence reached an asymptotic value, indicating maximum possible extension of the molecules. From a molecular model, Fuller & Leal estimate that their molecules were extended 25 to 50 times the size at rest. Concurrently, they developed a theory for dumbbell molecules with internal viscosity, variable hydrodynamic friction and nonlinear springs, and the model appears to fit the data when internal viscosity is neglected.

The research described in this section indicates that it is difficult to characterize non-Newtonian behaviour of polymer solutions in extension. Available measurements show that extensional viscosity depends not only on the local strain rate but also on the history of straining. An ideal fluid property is, of course, a material property and independent of the flow field. Still, some property must be found to indicate the magnitude of non-Newtonian effects in extension, for such a

property is necessary for applications like polymer flooding. It is apparent an important direction for research is to improve the characterization of polymer solutions in extension.

3. RHEOLOGICAL MODELS OF DILUTE SOLUTIONS

3.1 Overview of Molecular Modelling

Rheological theory for polymer solutions has generally been based on the dynamical behaviour of a single polymer chain in a flowing solvent or on the laws of continuum mechanics. In the latter approach, the premise is that the fluids follow the laws of continua, whatever the structure at the molecular level. In fact, the approach often leaves the impression that physical insight is deliberately avoided so that derived results have wide generality. Unfortunately, the generality usually brings with it a large number of material constants or material functions, too large to be found by experiment. This field of mathematical formalism was most active in the 50's and 60's and it failed to meet the needs of practising rheologists, typically a chemical engineer involved in rubber or plastics processing. There seemed to be little activity in this area in the 70's, probably because of the relative success of approaches based on molecular modelling.

The basis of the molecular approach is that there is a direct connection between forces at the molecular level with forces at the macroscopic level. Physically this is a natural approach, because a force at one scale is just the sum of forces at some finer scale. The problem then reduces to analyzing the forces at molecular level and then combining them correctly to yield forces, or equivalently, stresses at a larger scale.

At the molecular level; the relevant forces are easily identified but not so easily combined. The force tending to deform a molecule during flow is viscous drag and the restoring force is due to Brownian motion. While the statistical mechanics of Brownian motion are well established, there are various ways to determine the hydrodynamic forces, principally because the problem is one of calculating drag on curved, randomly-oriented segments of a continuous chain, the segments being in close proximity to each other. This mutual interference makes it difficult to determine local flow conditions from a known flow field outside the molecule.

The various ways in which this hydrodynamical problem has been tackled will be discussed in the ensuing sections. Whatever the method, the basic approach has been to analyze the dynamics of a single molecule, and then superpose results for application to solutions. This approach therefore strictly applies to dilute solutions, but it will be seen that the results are often applied to semi-dilute solutions and even used as a guide to rheological laws for concentrated solutions. The solutions of interest to EMR are semi-dilute at most, and so a thorough review of dilute solution theory is appropriate.

It is important to point out that there are two good reviews in the literature. Williams (1975) published an excellent survey in which he carefully analyzed the strengths and weaknesses of various molecular models. With 146 references, the review is intended to be the chemical engineer's guidebook to the literature on polymer modelling. Williams'

purpose was not to compare model predictions with experimental data, but to compare the models themselves. A similar review was prepared by Bixon (1976), but with polymer chemists in mind. While Bixon surveys much of the same literature as Williams, the treatment is less forceful, probably because Williams has published in this field and is more knowledgeable about details of the models.

Since the present review has a similar mandate, it is impossible not to retrace many of the steps of Williams and Bixon. It is also difficult to improve on Williams' penetrating analysis. Nevertheless, the prior reviews (i) do not include recent developments in nonlinear spring models, (ii) omit an important hydrodynamic model, the porous sphere, and (iii) make few comparisons with experimental results. This review will incorporate these topics, and will also be slanted to the aqueous polymer systems of interest to EMR.

As mentioned in chapter 2, the polymers of primary interest are polyacrylamide, polyethylene oxide and the polysaccharides. These polymers are long, linear (unbranched) and the first two form random coils. The polysaccharides form helices and behave like long rubbery rods. Because the dynamics are different, these polymers are treated separately, and we will continue to focus on flexible coils in this section.

3.2 The Rouse Theory and Bead-Spring Models

The cornerstone of dynamical theory for coiling polymers is the work of Rouse (1953). He showed how a long chain could be

analyzed as N subchains, set up the N equations of motion, and then found a way of solving the equations. To calculate the viscous force on each subchain, the segment is considered to be a sphere having the same drag force. Since Gaussian statistics are equivalent to a spring between each pair of spheres, the Rouse model and its derivatives have come to be known as bead-spring models. In essence, Rouse found that the behaviour of a random coil in shear is governed by a series of relaxation times, and that the largest and most significant ones are independent of the choice of N. Hence the artifice of subdividing the chain does not affect predictions of macroscopic quantities. Rouse solved the governing equations for an oscillatory flow field, primarily because that is usually the flow field when molecular theory is evaluated experimentally. In fact, in a separate but concurrent paper, Rouse & Sittel (1953) reported oscillatory flow experiments which verified predictions by the theory.

Rouse's theory applies in principle for all oscillatory frequencies, including $\omega = 0$ or steady shear. For this case, the theory predicts that the solution viscosity is constant, i.e., independent of the rate of shear. Since almost all dilute solutions are shear-thinning (aqueous solutions of PEO being a notable exception), the theory needed revision. The identified weakness of the theory was the neglect of hydrodynamic interaction between segments, and this led Zimm (1956) to supply the first major modification to the theory. Rouse assumed that solvent flow is unperturbed by the chain segments, an approximation which is questionable even for highly expanded coils. Hence, to

each chain segment, Zimm added a force which accounted for the disturbance to the flow by the two closest chain segments. Various degrees of influence could be incorporated, from none (the free draining case) to a maximum (the nondraining case). With the inclusion of hydrodynamic interaction, major differences were expected in the rheology. That turned out not to be the case, for the theory still predicts a constant viscosity in steady shear and yields relaxation times only marginally different from those of Rouse.

A flaw of the Zimm theory is that hydrodynamic interaction is preaveraged. That is, the interaction parameter is based on the average, and not the instantaneous, chain configuration. Even the preaveraged form requires numerical solution of the governing equations, and it is only recently that Zimm (1980) and Fixman (1981) have been able to estimate effects of fluctuating hydrodynamic interaction. Fixman reports that the intrinsic viscosity is 5% to 10% below that obtained with preaveraging, and that the change in the sedimentation constant is about 1%. Zimm reports percentages which are somewhat larger. Considerable computer time was required to obtain these results, and therefore that the preaveraged form of the Zimm and Rouse theories is still quite adequate. Other modifications have been made to Zimm's treatment of hydrodynamic interaction; Williams covers these in detail, but they seem much more relevant to polymer chemistry than to solution rheology. For example, Tschoegl (1963) introduced a parameter ε to account for excluded volume effects, i.e. to correct for the fact that a chain

configuration is not pure random flight because chain segments have finite volume and cannot occupy the same portion of three-dimensional space. With ε and the hydrodynamic interaction parameter h^*, much data from oscillatory shear experiments have been fitted to predicted curves by suitable choices of h^* and ε. But there seem to be few data from steady shear or other viscometric flows that have been fitted by the same two parameters.

As suggested above, molecular models are usually evaluated experimentally in an oscillatory shear flow. Some experimenters (notably Ferry) have made careers of testing solutions in this mode. In such tests, molecules are perturbed from their equilibrium configuration only a small amount and so at least two purposes are served: (i) by extrapolation, one can measure molecular properties in the equilibrium state, and (ii) if a molecular theory is being evaluated, one can accurately approximate non-equilibrium chain statistics in the theory with equilibrium statistics. Strain amplitudes can never be large in oscillatory experiments because polymer effects come into play only at frequencies higher than the inverse of the largest relaxation time – viz., generally above 10^3 Hz – and it is technically difficult to generate high amplitude motion at these frequencies. Hence in these tests, which supposedly determine the 'viscoelastic' properties of a fluid, molecules are deformed only slightly from their average spherical shape. However, practical flows are usually steady flows and then molecular deformations may be quite large. Because such flows provide a

more severe test of a molecular model, subsequent comparisons will therefore emphasize steady flow data.

3.3 Internal Viscosity

The addition of hydrodynamic interaction to bead-spring models was essentially an attempt to account for the impermeability of a polymer coil. Zimm's (1956) method of dealing with hydrodynamic interaction was physically reasonable, but another approach was developed at about the same time. The approach was based on the concept of internal viscosity, and the mathematics was developed by Cerf (1957). The concept supposes that chain segments resist deformation not only because of Brownian motion but also because of the time required to change conformation. This latter resistance is thus dependent on the rate of deformation of a coil, in contrast to Brownian motion forces which are proportional to deformation itself. Because this new resistance is proportional to rate, it is similar to a viscous resistance and because it applies to chain segments, it is an internal type of viscosity. The concept is actually a reflection of chain flexibility, but the term viscosity correctly infers the linear dependence on rate of change.

Because of this proportionality, the mathematical problem for the N-bead chain is still linear and so Cerf was able to solve the dynamical equations. The results naturally include an additional parameter, the coefficient of internal viscosity ϕ. Further developments to the theory, made by Peterlin, Williams,

and by Cerf himself (see Williams, 1975) considered symmetry of the stress tensor, angular rate of notation of chain segments in shear flow, and the relation of ϕ to atomic properties. A good analysis of these developments is given by Bazua & Williams (1974).

The literature furnishes little information which facilitates direct comparison of experimental data to predictions which incorporate internal viscosity. The oscillatory shear data of Massa et al (1971) and Osaki & Shrag (1971) are well correlated by parameters from the theory, as Williams (1975) reports, but there seems to be no other supporting evidence from oscillatory shear experiments. Perhaps the strongest support comes from the results of Cottrell et al (1969) for steady shear, a flow which provides a severe test. Using light scattering, they measured the deformation of polyisobutylene molecules at shear rates up to 600 s^{-1}. For their polymer sample, these rates were up to 50 times that needed to initiate molecular deformation, i.e., 50 times the inverse of the largest relaxation time. Their data are compared with predictions for the free-draining and nonfree-draining bead-spring models and the measurements of deformation are two orders of magnitude below the lowest predictions. Comparisons with Cerf's theory for nondraining coils with internal viscosity are much better, for his theory predicts at least the right order of magnitude.

The most penetrating study of internal viscosity is by Zimmerman & Williams (1973). They subjected four internal viscosity models to a demanding test: predictions from the models

were compared with stresses measured in oscillatory shear and steady shear. None of the models was able to fit non- Newtonian data from both shear flows. It may be argued that these comparisons are not a fair test because the solutions (polystyrene in Aroclor) were far from dilute and the theories apply to dilute solutions. Zimmerman & Williams conclude that the models are not even useful for engineering purposes, even though they acknowledge that the models are superior to the simpler Rouse-Zimm models.

Their assessment appears to be the last word on the subject. The only significant article since then which deals with internal viscosity is the work by Fuller & Leal (1981). They analyzed the dynamics for a very general dumbbell model having variable friction, nonlinear springs, as well as internal viscosity. However, their birefrigence data (Fuller & Leal, 1980a, 1980b) are best correlated when the internal viscosity parameter in the model is zero, as was reported earlier in section 2.2.

All in all, then, internal viscosity seems to improve molecular models but a satisfactory model has yet to be found.

3.4 Nonlinear Springs

Most of the work on molecular modelling during the past decade has centered around nonlinear springs. It will be recalled that the spring represents Brownian motion forces on a segment, and a linear spring accurately reflects the restoring force provided molecular deformation is small. That is, the

linearly elastic spring follows directly from Gaussian chain statistics, which are valid at states near equilibrium.

Nonlinear springs were proposed when it was realized that linear spring models – the Rouse-Zimm models – predict wholly unrealistic stresses in steady elongational flow. While failure of these models to predict non-Newtonian behaviour in steady shear received considerable attention for some time, it was eventually recognized that the more important failing is that the stress in the straining direction can increase without limit in steady elongational flow (Walsh, 1967). This behaviour follows from the fact that, once the molecule is deformed from equilibrium, viscous forces in an extensional flow increasingly dominate the restoring forces. In a steady state situation, then, there is no time limit for molecular extension and consequently the deformation and the induced stress are unbounded. Theories for the 'uncoiling' of a macromolecule in an extensional flow were developed independently by de Gennes (1974) and Hinch (1975). While their analyses are useful in explaining how molecules might become extended enough to affect shear stresses in turbulent flow – viz., to explain the phenomenon of drag reduction – they are not useful in predicting normal stresses in extensional motions.

Steady state extensional flow is an ideal which cannot be created physically. In a realistic flow, such as a converging flow, the extensional motion is convected and the time available for molecular stretching is finite. King (1977, 1982) showed that the Rouse model is valid <u>in principle</u> in converging flows,

and found that the additional normal stress in the straining direction is comparable to the extra tangential stress in shear flow (which is just the increase in viscosity and is therefore small). Experiments on converging flow, e.g. James & Saringer (1980), however, showed that the additional normal stress is not small; in fact, it is several orders of magnitude above Rouse model predictions. Hence, King's analysis reconfirms the need for bead-spring models which are realistic in extensional flow.

As suggested by the title of this section, one means of improving bead-spring models is to introduce nonlinear springs. Because of intramolecular entanglements, or even because of finite chain length, molecular extension is limited and so springs with finite length would be more appropriate. Such a spring is necessarily nonlinear, the spring constant increasing with displacement.

The main contributors to the work on nonlinear springs have been Tanner, Bird and their co-workers. There were prior attempts but the most worthwhile work was started by them in 1971. Tanner & Stehrenberger (1971) proposed two nonlinear springs, one being the 'Langevin spring', in which the force-displacement relation is given by the inverse Langevin function, and the other being a 'linear locked' spring in which the spring deforms as a linearly elastic connector until a certain length is reached at which point the spring locks. Tanner & Stehrenberger investigated dumbbell models with both types of springs in an elongational flow field and found similar results at high strain rates, namely, an upper bound on normal stress. They studied

only the linear-locked model further because the associated mathematics are easier. They also limited their study to the dumbbell because of complexities with the N-bead model. As for shear flow, they found the viscosity decreased with shear rate in a wholly realistic fashion and normal stress values were realistic as well. While the models proposed by Tanner & Stehrenberger have the correct viscometric behaviour, the unsatisfactory aspect is that for a general N-bead chain the calculations depend on the choice of N (in contrast to Rouse-Zimm theories with linear springs).

Tanner (1975a) continued investigating the dumbbell model, finding the constitutive relation for a dilute solution of non-linear dumbbells. He then modified the model to include a non-constant friction coefficient (Tanner, 1975b), which added an adjustable parameter and complicated the mathematics. The main benefit of the modification was to generate a hysteresis loop in extensional flow – a feature sought to assist in the explanation of drag reduction. But again, stress levels depend on the parameter N.

When Tanner & Stehrenberger introduced the inverse-Langevin-spring model in 1971, Stevenson & Bird (1971) investigated the same model in the same flow. They too made calculations for the dumbbell and they found the same results: the normal stress in steady elongational flow increases rapidly with strain rate and then approaches an upper bound. Their paper is noteworthy because the model was the precursor for the well-known FENE model. FENE stands for finitely extendible nonlinear elastic,

and the force-displacement relation for a FENE spring is similar to the inverse Langevin function but algebraically simpler. The FENE model was proposed by Warner (1972), who analyzed a dilute solution of dumbbells with FENE connectors. He found the viscosity and first normal stress difference in steady shear flow, analytically for small shear rates and numerically for the full range of interest. He also predicted viscometric behaviour in oscillatory shear flow and found curves qualitatively similar to experimental data. Armstrong (1974a, 1974b) continued the analytical work to higher powers in the strain rate, i.e. beyond Warner's first order solutions. Analysis for oscillatory shear was continued by Christiansen & Bird (1978) and solutions were found for large and small frequencies. In their paper, they usefully compare FENE dumbbells of various stiffness with rigid dumbbells, Hookean dumbbells and with prolate ellipsoids with different axial ratios. This graph is reproduced on the next page. Predictions of reduced intrinsic viscosity were then plotted alongside considerable experimental data – a sample is shown on the next page – and it becomes apparent that a FENE dumbbell, with a properly chosen spring parameter b correlates steady shear data better than other models. The picture is different, however, for unsteady shear. Results of complex viscosity were simply not well correlated by the FENE model, for any value of b. This discrepancy is not unexpected in the sense that the FENE model was developed for the large deformations of extensional flow and not perturbations about equilibrium. On the other hand, the FENE model reduces to the Hookean model as

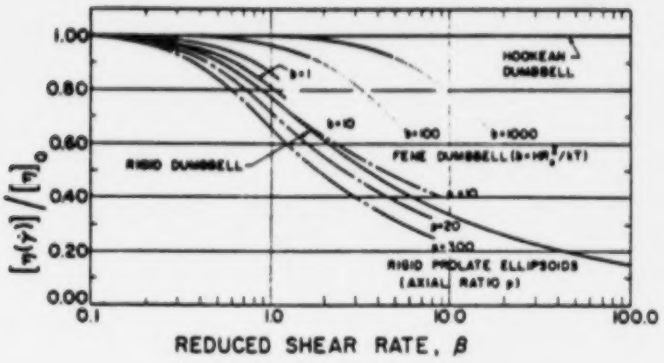


Fig. 1 from Christiansen & Bird (1978). The ordinate is the intrinsic viscosity at a finite shear rate relative to that at zero shear rate. The abscissa is the product of the shear rate and a fluid relaxation time (which is close to the first Rouse relaxation time). The graph compares predictions from a number of models, including rigid particles.

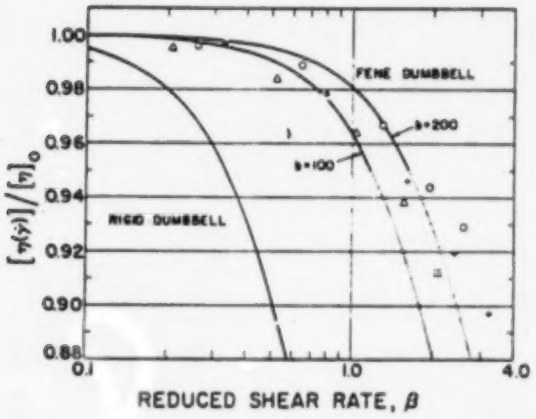


Fig. 3 from Christiansen & Bird (1978). The solid curves are predicted from the FENE dumbbell model for different values of the spring resistance parameter b, i.e. for b = 0, 100 and 200. Experimental results are for polystyrene ($\bar{M}_w = 10^7$) in toluene at different temperatures.

$b \to \infty$, and it has been well established that the Rouse-Zimm model with elastic springs is accurate in oscillatory flows. The resolution of this dilemma probably lies in the fact that Christiansen & Bird's predictions are for a dumbbell model, while the Rouse coil is an N-bead model.

The FENE model is carried to completion, or close to it, in Bird et al (1980). In this work, the model is extended in three ways: hydrodynamic interaction is incorporated à la Zimm, the spring displacement relation is pre-averaged à la Peterlin (and so the spring is termed FENE-P) and the analysis is extended to the N-bead necklace. Solutions of the dumbbell and the N-bead chain are given for steady shear, steady elongation, small-amplitude oscillatory shear and shear relaxation. The improved models yield the correct, or desired, non-Newtonian behaviour in these four flows. Then the N-bead model is fitted to experimental results, and this time the oscillatory shear data, as well as the steady shear data, are well correlated by the model. This improvement over the attempted correlations by Christiansen & Bird can likely be ascribed to the inclusion of hydrodynamic interaction and the extension to N beads. These modifications introduce two parameters, additional N and h^* (the usual dimensionless parameter for hydrodynamic interaction), and so the model now contains three adjustable constants: N, h^* and b. With three parameters available, it is perhaps less surprising that the model can be fitted to a variety of experimental results.

There is little doubt that the FENE or FENE-P model is the best one available for describing the non-Newtonian rheology of

dilute solutions. Yet the critical test of the model has not been made, or has not been reported. All nonlinear spring models were developed to predict correct behaviour in extensional flow. The real test is whether the parameters which correlate data for shear flow correlate data for elongational flow as well. When this test is done, the report card on the FENE model will be complete.

3.5 Rheology of Suspensions

In the discussion of nonlinear spring models, there was reference to models of rigid particles. The linear-locked spring dumbbell of Tanner and Stehrenberger (1971) is in fact a rigid particle once the spring has been extended to its limit. Moreover, in the figure extracted from Christiansen & Bird (1978) on page 40, there is a comparison of the FENE model to a rigid dumbbell and prolate ellipsoids. This treatment implies that a solution of macromolecules is equivalent to a suspension of rodlike particles. Although particles and coiled macromolecules differ greatly in flexibility, the analogy is apt because at high strain rates molecular extension is limited by self-entanglement, and then the hydrodynamic forces on a molecule are equivalent to those on a long particle. Consequently, we will take a brief look at the rheology of suspensions in this section, paying particular attention to suspensions of long particles.

Suspension rheology is an active field of research, particularly for applied mathematicians. Because particles are

small and the Reynolds number is therefore low, and because the suspending liquid is Newtonian, the governing equations are linear and thus amenable to solution. Hence physically-oriented applied mathematicians like Batchelor, Bird, Brenner, Hinch and Leal have made great contributions to suspension rheology in the last dozen years.

One particle which is directly related to macromolecular dynamics – in fact, it is taken as a model for rodlike molecules – is the rigid dumbbell. A thorough review of the rheology of dilute suspensions of dumbbells, in which the dumbbells are subjected to Brownian motion as well as to hydrodynamic forces, was furnished by Bird et al (1971). Non-Newtonian stresses were worked out in detail for a variety of flows, and comparisons made to experimental data show good agreement for steady shear but not for oscillatory shear. Armstrong and Bird (1973) continued the analysis to find integral expressions for the stress tensor, but the equations do not appear to be more useful than those given in the prior review paper.

As for particles of more general shape, the state of the art has been summarized by two review articles. The better one is by Brenner (1972), whose twenty years' experience and systematic approach have led to a well organized, knowledgeable review. The review is also comprehensive, for it includes dumbbells, liquid droplets and gas bubbles. The other review is by Jeffrey & Acrivos (1976), which has the advantage over Brenner's review, at least for our purposes, of a fuller treatment of Batchelor's long-particle theory.

As in polymer solution rheology, the flows of primary interest are simple shear and pure extension (no mention of oscillatory shear in the suspension literature). Rheological effects in each flow will now be discussed in turn.

In shear flow, the fundamental work started with Jeffrey (1922) who solved for the motion of an ellipsoid of revolution in simple shear, neglecting Brownian motion. Scheraga (1955) added Brownian motion and showed that dilute suspensions were shear thinning, but had Newtonian viscosities at very high and very low rates of shear – identical to the behaviour of dilute polymer solutions. Scheraga's results demonstrate that the degree of non- Newtonian behaviour increases as the aspect ratio increases, as might be expected.

In shear flow, particles tumble in the rotational flow field but spend most of their time oriented nearly parallel with the streamlines. In extensional flow, the particles are quickly aligned in the direction of flow and this orientation produces the maximum hydrodynamic effect, in contrast to the effect in shear. There are two theories which treat particles in an extensional flow field. Batchelor (1971) predicts stresses produced by a 'non-dilute' suspension of elongated particles in a pure straining field. Since the analysis deals with particles already aligned, it applies to threads and other deformable long particles as well as to rods. His analysis shows that the additional normal stress is proportional to the velocity gradient and to the square of the particle aspect ratio. For a dilute concentration of .001 by volume, and for an aspect ratio

of 10^2, his results show that the normal stress is O(10) higher than the Newtonian viscous stress. This finding is significant because it was the first analysis to show how long particles are capable of generating large stresses in an extension flow field. Batchelor's predictions have been confirmed to a good degree by the experimental data of Weinberger & Goddard (1974), Mewis & Metzner (1974) and Kizior & Seyer (1974).

The other theory regarding long particles in extensional flow is by Brenner (1972). His particles are ellipsoids of revolution – prolate spheroids with aspect ratios s greater than one and oblate spheroids with s less than one. By analyzing the flow around a single particle, he finds that the increase in tensile stress is proportional to the velocity gradient and to s^2, the same dependence which Batchelor found. The two theories, which are both approximations, differ slightly in the proportionality constant and in the dependence on concentration. But the theories agree in substance, and so they provide useful estimates of non-Newtonian stresses for extensional flows containing long or elongated particles.

3.6 Porous Sphere Model

A wholly different approach to modelling the hydrodynamics of a polymer molecule is to consider the random coil as a porous body. In many molecular models – particularly, the bead-spring necklaces of Rouse and Zimm – it is assumed that the flow of solvent is unperturbed by the polymer chains. In a shear flow,

for example, this assumption means that the velocity gradient is constant inside as well as outside the molecular coil. Intuitively this seems wrong, because one expects the flow in the interior to be slowed down by chain segments. A model which overcomes this defect is the porous sphere model, although it has its own shortcomings.

The porous sphere model was developed independently by Brinkman (1947b) and Debye & Bueche (1948). To describe flow inside and outside the porous body, both proposed the same governing equation, which is a combination of Darcy's equation for porous media flow and Stokes equation for low Reynolds number flow. They and subsequent researchers have solved the governing equation to predict two quantities of particular interest: the intrinsic viscosity of a dilute solution and the friction coefficient of a single molecule. The paper of Debye & Bueche (1948) is really a joining of two separate contributions: Debye solved for the intrinsic viscosity of a dilute suspension of porous spheres of uniform permeability and Bueche found the drag force on a single porous sphere as it moves at constant speed through a stationary solvent (as happens in sedimentation). In each case, the prediction was checked by letting the permeability approach zero and comparing the result to the known result for a solid sphere. For the suspension, the viscosity approached Einstein's well-known relation for a suspension of spheres, and for the single sphere, the drag approached Stoke's law for a sphere. Brinkman (1947a) proposed the same governing equation as Debye & Bueche then solved for the friction coefficient f and the intrinsic viscosity $[\eta]$ of a

suspension of uniformly porous spheres (1947b). His results appear to be the same as those of Debye and Bueche; his solutions have a different functional form, but they have the same asymptotic limits at infinite and zero permeability.

The next major attack on the problem came from Mijnlieff and his co-workers in the Netherlands. They focussed on the assumption of uniform permeability, which is not wholly realistic for a macromolecule whose segment density increases toward the centre. First, Ooms et al (1970) developed a numerical technique to find the frictional coefficient for a sphere with radially varying permeability. Later, Wiegel & Mijnlieff (1977) and Mijnlieff & Wiegel (1978) analytically solved for the case of sphere with permeability varying as $\exp(ar^2)$, where a is a constant and r is the radius. In their papers, they show how this variation follows reasonably from the known exponential variation of polymer segment density. For this variation, they predict $[\eta]$ and f for polymer-solvent systems in which the macromolecular size is known as a function of molecular weight. Comparison with measurements shows excellent qualitative agreement and good quantitative agreement. What is not shown, unfortunately, are corresponding predictions based on uniform permeability.

Wiegel (1979) worked on the equivalent two-dimensional problem, the infinite circular cylinder. Assuming homogeneous permeability, he found the frictional resistance for rotation as well as that for translation. Details for the latter case were

not given, which is regrettable because the results may be used as a first step in the study of hydrodynamic effects with long rodlike polymers, particularly polysaccharides.

The porous sphere problem was also tackled by McDonnell & Jamieson (1980). Like the Dutch group, they solved the Debye-Bueche-Brinkman (DBB) equation for spheres with exponentially-varying permeability. Their work is similar to prior work, and they end up reinterpreting predicted results and testing them against new experimental data. The agreement between prediction and measurement is good, including data for biological polymers.

The most recent paper on the porous sphere model, by Johnson and Segalman (1981), is the most complete but the least original. Once more the DBB equation is solved for a sphere in translation or in rotation in a shear field, and again for both uniform and exponentially-varying permeability. The main value of the paper lies in the complete mathematical development, quite in contrast to the original work of Debye & Bueche (1947) who present final results without any details of the method of solution.

An essential aspect of the porous sphere model is the rigidity of the particle. In sedimentation, this assumption is not unreasonable because the external flow is uniform and there are no large velocity gradients tending to deform the coil. In shear flow, however, the assumption of a rigid sphere is valid only for low shear rates or small molecules. It should be noted that in a shear flow the porous sphere rotates at a constant

angular velocity which is half the velocity gradient, just as a solid sphere does. This rotation determines the extra viscous dissipation and thus the increase in viscosity or the intrinsic viscosity. Molecules will behave as rigid porous bodies when the segment density is high, i.e. the molecule is compact, and when deformation is small, i.e. at low shear rates. Unfortunately, these conditions of low shear and compactness are not appropriate for the polymers which are used for hydrodynamic effect; viz., applications almost always require large, easily-deformed molecules and the shear rates are rarely small because industrial flow processes are generally more economical at high flow rates.

Hence, the porous sphere, as it stands, is not expected to be a useful model in most rheological applications. However, the idea of modelling the interior of a random coil as a porous medium is obviously a good concept, and an apparent direction for future research would be to combine this concept with a deformable coil. This task would not be easy, for it is a typical problem in coupled effects: i.e., flow rate through the coil is determined by its configuration, but the configuration is determined by the flow. However, this situation is no worse than any other coupled problem and resolving it gets to the heart of the problem in modelling polymer dynamics.

4. CONCLUSIONS AND DIRECTIONS

4.1 Conclusions

1. For the polymer solutions of interest to EMR, specifically dilute and semi-dilute solutions of polyacrylamide, polyethylene oxide and polysaccharides, the rheology is well characterized in shear but not in extension. The most pronounced non-Newtonian behaviour of these fluids is in fact in extension, for hydrodynamic effects are two orders larger than those in shear, but proper characterization in the extensional mode is still in the formative stages.
2. Preparation of solutions of polyacrylamide and polysaccharides must take into account the ionic strength of the solvent, because hydrodynamic effects produced by these polyelectrolytes are highly sensitive to ions in solution.
3. Various molecular models are available for simulating the dynamics of a randomly-coiled chain. Of these, the best developed and most promising is the FENE (or FENE-P) model of Bird and company. This model is elaborate, for it incorporates nonlinear springs and hydrodynamic interaction in an N-bead necklace, but it appears to correlate steady and oscillatory shear flow data. No model, including the FENE, has been shown to correlate data from both shear and extensional flow.
4. Incorporation of internal viscosity in a molecular model does not seem to lead to better agreement with experimental results.

5. Porous sphere models are limited because they are rigid. Rheological use is hence constrained to compact molecules at low rates of deformation.

4.2 Directions for Future Research

1. Light scattering experiments are needed to determine molecular deformation and motion. There is a wealth of theoretical work on the motion of macromolecules in a flowing solvent, but little solid experimental information. It is not clear, for example, how much molecules extend in simple shear flow and what is the nature of their motion, viz., is their behaviour closer to that of liquid droplets or of rigid rods? Without knowing how a molecular coil rotates in a shear flow, it is very difficult to begin modelling the dynamics. Analogous to Fuller & Leal's experiments for stationary elongational flow, it would be useful to measure molecular deformation by light scattering for convected extensional motion in a well-defined flow field.
2. Ways must be found to properly characterize the extensional resistance of dilute solutions. The problem is one of having a measurable effect in a flow where both the deformation field and stress field are well defined. A promising flow field in this regard is converging channel flow at high Reynolds numbers.
3. The porous sphere model is an attractive approach to molecular modelling if coil deformability is added. This

approach has not been attempted before and is admittedly difficult because the problem is a coupled one, as described in section 3.6. However, the problem is tractable, no more difficult than other molecular models, and therefore well worth pursuing.

4. Molecular extension is limited apparently because of intramolecular entanglements. In principle, it should be possible to incorporate entanglements in the mechanics and thus predict non-Newtonian properties at high rates of strain. The associated mathematics would be useful not only for a single molecule but also for entangled molecules in non-dilute solutions. This approach could lead to significant advances in rheology for a wide range of polymer solutions.

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SURVEY OF HYDRODYNAMIC EFFECTS WITH MACROMOLECULES

C. FLOW OF POLYMER SOLUTIONS THROUGH POROUS MEDIA

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1. INTRODUCTION

1.1 The Use of Polymers in Enhanced Oil Recovery

While polymers have been used for 30 years in enhanced oil recovery, it is only in the last decade that the associated physical and chemical processes have been clearly identified. The mechanisms are introduced in this first chapter without reference to the literature, and detailed discussions and supporting references are left to later chapters.

Polymer flooding, or the introduction of a polymer slug in water flooding, has become a well-established but not common technique for enhanced oil recovery. The technique was developed to improve water flooding, a secondary recovery method applied to half the reservoirs in North America. When water is used to displace oil left after primary recovery, the water tends to 'finger' its way through the pores, leading to early breakthrough of water at the collecting well. Polymers are added to lower the mobility* of the water, closer to that of oil. Originally, polymers were used because of their known ability to increase viscosity; in fact polymers are commonly sold as thickening agents because a high-molecular-weight species can increase the

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* Mobility is the ratio k/μ from Darcy's equation for porous media:

$$V = \frac{k}{\mu} \frac{\Delta p}{\Delta x}$$

where V is the superficial velocity, k is the permeability of the medium, μ is the viscosity of the fluid, and $\Delta p/\Delta x$ is the pressure gradient.

viscosity by a factor of ten or a hundred, at concentrations of only 0.1%. Hence the idea was to add polymer to thicken the water and consequently reduce fingering. However, laboratory studies showed that the pressure drop could be much higher than the increase in viscosity, and particularly so at high flow rates. The high-rate resistance was identified as a viscoelastic effect, a finding which generated considerable interest in the rheology community. However, the necessary high flow rates generally occur only around the injection well and hence the effect, although highly beneficial, is not significant overall.

Further studies showed that additional resistance in porous media flow was caused by polymer adsorption. That is, polymer reduces mobility by increasing the viscosity, as already noted, and also by reducing the rock permeability through adsorption. Polyacrylamide, the polymer most often used for polymer flooding, is a polyelectrolyte with a strong affinity for the surface of sandstones. A layer of adsorbed polymer on the surface effectively reduces the permeability, and the reductions can be significant because the layer thickness is comparable to the pore size.

The strongest competitor to polyacrylamide is Xanthan gum, one of the polysaccharides. Research with this polymer is increasing, for it does not degrade as easily and is less sensitive to salinity of the solvent. However, polysaccharides are more expensive and their effect appears to be mainly viscous.

Some additional effects of polymers in porous media flow have been detected. These effects are referred to as:

(1) hydrodynamic retention; molecules are retained in the porous medium by a flow-induced diffusion to stagnant zones, the retained amount increasing with flow rate; (2) inaccessible pore volume; when polymer molecules are too big to enter all pores, a portion of the medium is inaccessible to polymer flooding; (3) mechanical entrapment; large molecules are irreversibly trapped in small passages, increasing the amount retained by the medium above that due to adsorption; (4) steric exclusion; because the closest a molecule can approach a wall is half its diameter - or half its length in the case of the rodlike polysaccharides - the concentration of polymer is less near the wall and consequently the bulk viscosity of the solution is lowered. These four effects are certainly interrelated, and the thrust of current polymer research is to understand the basic physics of each effect and hence to anticipate their combined effect in the field.

1.2 Organization of the Report

The search for all relevant literature for this review started with the author's own collection. The collection was expanded by working backward and forward in time - backward via the bibliographies of the collected articles, and forward via the Citation Index. To confirm the thoroughness of this library search, an entirely independent search was carried out with the aid of the computer. The latter exercise turned up a few additional papers - none significant - and in all about 250 works

were gathered. By these combined searches, it is unlikely that a major development has been overlooked, and so this survey should accurately reflect the present state of knowledge regarding polymers and porous media flow.

This survey was written for personnel at the Coal Research Laboratory (CANMET-EMR) at Edmonton, Alberta, and is intended to help guide the polymer research program of the Laboratory. It is assumed that the reader has a background of physics and chemistry and an acquaintance with fluid mechanics and rheology. Some terms particular to the oil industry will be introduced as needed.

To organize this survey, the 250 papers were sorted according to major topic. The papers generally cover more than one topic, but most deal with one main topic, and so it was straightforward to clasify papers accordingly. Papers in each category are discussed together in a chapter of this report. When a paper contributes significantly to another topic, it is discussed in that chapter as well, but there has been no attempt to mention every paper that contributes to a topic if that paper is already discussed in another chapter. Hence the purpose of each chapter, like that of the report, is to cover the main developments and not to reference every article. A consequence of this approach is that not all 250 papers are mentioned in the text. All are listed in the Bibliography, and about 200 of these have been used for discussions in the text.

2. REVIEW ARTICLES

About a dozen review articles on polymer flooding have appeared in the literature and they are separated here into surveys and overviews. The former category is for articles which are comprehensive reviews of the literature, while the latter has been reserved for usually shorter articles of an introductory or explanatory nature.

2.1 Surveys

The first survey on polymer flooding was by Savins (1969), an engineer involved in polymer applications at Mobile Research. The emphasis of his review, comprising 185 references, was the relation between the rheology of a polymer solution and its non-Newtonian behaviour in porous media. This concern is understandable because two years earlier, Marshall & Metzner (1967) and Dauben & Menzie (1967) had clearly demonstrated that viscoelastic effects occur in porous media flow. Hence Savins spends some time discussing rheological models for polymer solutions and leaves to shorter sections discussions of the equally important effects of adsorption and blockage. His description of field tests are brief as well. Despite this imbalance, the article found great use because it was comprehensive, authoritative, and the first of its type.

The next review, a year later, was an ideal complement to Savins' study. Jewett & Schurz (1970) reviewed the performance

of 61 polymer flood projects undertaken between 1964 and 1969. All relevant field conditions are given, including reservoir conditions and prior recovery operations, and the authors rate the success of each project. By noting the conditions common to success or to failure, the authors identify the circumstances when polymer flooding is likely to be worthwhile.

Jewett & Schurz' review was directed to field operations, as was the first major review from the Canadian Petroleum Institute, by D.H. Stright (1976). Stright's review is much more comprehensive; he includes polymers other than polyacrylamide, discusses the characteristics of each polymer, describes the various interactions as polymer flows in a porous medium, warns of handling problems and incorporates laboratory findings. Because the report is intended for reservoir engineers, even field equipment is described, including a pump-pipe layout. Stright carefully shows how nonionic polyacrylamide and polysaccharides work by increasing the viscosity of the solution, while partially hydrolyzed polyacrylamides reduce mobility by adsorption as well. Because of these combined mechanisms, Stright concludes that this polymer offers a cost advantage over polysaccharides. Also included is a long section on the 100 field tests that had been conducted up to 1976, including the 61 covered by Jewett & Schurz. In all, Stright offers the best single review on the use of polymers in enhanced oil recovery.

The most recent review appears to be by Chang (1978). His evaluation of field tests includes a detailed look at sixteen field operations, and he provides some non-technical details as

well, even listing the costs and durations of flood projects (up to $65M and two years). Like prior reviews, Chang cites the reservoir conditions and polymer conditions that are most likely to produce a successful flood.

2.2 Overviews

There are a number of papers which review polymer flooding, but which should be termed overviews. The general purpose of these articles is to introduce the reader to the terminology, the physical chemistry, the underlying mechanisms, and the relative importance of each factor. The articles usually attempt to describe the field completely, but there is no attempt to incorporate every relevant paper, as in a proper review. Overviews often appear in trade magazines, but the ones included here are from engineering or scientific journals.

One of the earliest overviews was by White et al (1973). Like writers of survey papers, White and colleagues suggest guidelines for designing and managing a polymer flood, but their essential message is that polymers will not be effective in all cases. The banner year for overviews was 1977 when no less than four appeared. In terms of scope, perhaps the best one is by Sandiford (1977), a well-known petroleum engineer who has published extensively on polymer flooding. Another one, by Stanislav & Kabir (1977), is a good introduction for the casual reader but leaves the impression that the writers are not familiar with the topic. The third is by a leading rheologist,

Metzner (1977), who covers most of the relevant mechanisms but whose main thrust is to explain hydrodynamic retention by molecular thermodynamics. The fourth is an excellent review paper by Sandvik & Maerker (1977) on polysaccharides. At that time, Xanthan was just emerging as a strong candidate for polymer flooding, and their paper is primarily devoted to comparing performances of that polymer with the commonly used polyacrylamide.

Probably the best recent overview on all enhanced recovery processes is that by Johansen (1979). He explains not only the usual fluid displacement processes covered in this report - water, polymer, micellar and surfactant flooding - but also the thermal recovery processes and miscible-fluid displacement techniques. It is an excellent primer on current practices in oil recovery.

Some other overviews have appeared and should be noted. Articles by Baijal & Dey (1978), Burtch (1981), and Taber & Martin (1981) are all short, four to seven pages, but all make satisfactory use of the space taken.

It is apparent that the recent articles have focussed more on field tests or directly applicable laboratory tests, and relatively little attention has been paid to fundamental research. Because of this and because of the interests of EMR and the writer, the emphasis in the present review is on the fundamental side.

3. LABORATORY STUDIES OF POLYMER FLOODING

3.1 Early Papers

The primary purpose of this first section is trace the initial reporting of polymer flooding in the technical literature. Since most of the early articles emphasize field studies and are general in nature, there is no clear distinction between them and some of the review articles in the previous chapter. Moreover, some early articles include laboratory work, particularly on reservoir models, and so some of these articles might logically have been discussed in the subsequent section of this chapter.

The first reference to polymer flooding appears in the U.S. Patent literature. Patents as early as 1944 describe methods for recovering residual oil, but polymers are not mentioned until the mid 1950s. The Patent abstract of Binder et al (1952) refers to the injection of a "viscous aqueous solution having a viscosity of about 100 to 1000 centipoises ...". Since water is thickened most easily by a polymer, the injection liquid is likely a concentrated polymer solution. The first reference to polyacrylamide is in the Patent abstract of Sandiford et al (1956). The abstract specifies, among other things, that the polymer have a molecular weight such that the viscosity of the flood liquid is between 1 and 1000 cp. These numbers provide some idea as to how much viscosity enhancement the petroleum engineers were looking for in those days.

3.2 Laboratory Models of 5-Spot Patterns

The first journal article on polymer flooding appears to be by Barnes (1962). To demonstrate how polymers improve oil recovery, he and others developed two-dimensional flow cells to represent the conditions in fields where wells are arranged in a 5-spot pattern. (In this pattern, collection wells form a square grid and an injection well is located at the centre of each square). The laboratory equivalent is a shallow sand pack, square in plan, with impermeable but transparent walls top and bottom, and with impermeable walls on the four vertical faces. When fluid is injected at a well in one corner and collected at a well in the opposite corner, the resulting two-dimensional flow pattern simulates flow in a quarter of a 5-spot pattern. By making the displacing fluid and the displaced fluid different colours, the interface between the two fluids is visible, and the model graphically demonstrates how polymers reduce fingering and improve sweep efficiency. These effects are clearly illustrated, for example, in pictures taken by Lee & Claridge (1968). Slater & Farouq-Ali (1968, 1970) also used the 5-spot model to test their predictions of oil recovery and sweep efficiency. They developed equations to describe the flow resistance and, by finite difference techniques, computed flow behaviour which was found to agree well with data from their 5-spot model.

3.3 Early Tests on Cylindrical Cores

Because the flow pattern in the 5-spot model is two-dimensional, it is not useful for determining basic properties of porous media like flow resistance. A linear flow in a homogenous core is much more suitable for such work and hence almost all laboratory studies have been conducted on cylindrical cores of reservoir-type rock. In this section, papers up to 1971 are reviewed and later papers are reviewed in Section 3.6.

The first tests on cylindrical cores are described in back-to-back articles in the Journal of Petroleum Technology. Pye (1964) measured the flow resistance of polymer solutions in porous media and found an apparent viscosity much higher than the measured solution viscosity. This appears to be the first realization that polymer had a beneficial effect other than by augmenting the viscosity. Sandiford (1964) also concluded that there was extra mechanism which reduced water mobility but his experiments, which measured oil recovery and not flow resistance, show this less directly. This additional polymer effect was traced to polymer-rock interactions, and Smith (1970) conducted systematic tests to determine how polymer adsorption depends on salinity, pore size, molecular weight and flow rate. He found that the amount of adsorption increased with salinity, but that increased salinity lowered the polymer's effectiveness in reducing mobility because of the smaller molecular size.

Further work on adsorption and solution rheology were carried out by Mungan (1971) and Jennings et al (1971), but even though each measured the shear viscosity over a wide range of conditions, the separate influence of rheology and adsorption is not made clear. Mungan measured adsorption by direct mass balance and found that the amounts varied from 30 to 220 micrograms per gram of rock (these units, μg/g, have become standard in the industry). While these amounts are small, Mungan showed that the cumulative effect is not, and that the concentration of the polymer slug should be increased significantly to compensate for the lost polymer.

3.4 Cost Analyses

Polymer flooding is economically viable only if the extra oil produced by the polymer more than pays for the cost of injecting it. Cost accounting is outside the scope of this report and is usually not a direct factor in scientific research on polymer flooding. Yet cost is the only criterion for the producer and some papers in the technical literature deal with this aspect. Articles which give the actual costs of managing a flood are quite revealing. Chang (1978), for instance, reports the breakdown of costs of two typical reservoir operations: for one, a Xanthan gum flood, the cost of the polymer alone was 65 million dollars.

Other articles have predicted improved reservoir output due to polymer flooding. Patton et al (1971), for example, predicted

the return of incremental oil per dollar of polymer injected for a California-type reservoir, based on a numerical model and on laboratory core data. Still other papers have dealt with the economics of specific parts of the operation. Szabo (1979) measured the shear viscosity of a large number of candidate polymers and evaluated their performance partly on the basis of the increase in viscosity per dollar of polymer. Uzoigwe et al (1974) investigated the shape of the polymer slug and, relying on Mungan's (1971) data, showed the economic advantage of a programmed slug over a conventional square one.

When economics are discussed in overview articles, the clear message is that polymer flooding is not economical in all cases. The successes have generally come by carefully matching the polymer to the reservoir; however, because of reservoir variabilities, even the most thorough laboratory program does not always lead to a profitable polymer flood.

3.5 Field Tests

Articles in the open literature on polymer flooding generally deal with laboratory work and not with field tests. This is quite understandable, because laboratory data can be applied to a number of situations, whereas field results generally cannot be transferred to another situation. Moreover, oil companies are competitive and therefore reluctant to share field information. However, some reports of field studies are published in engineering journals and some examples are presented

here. One of the earliest was a detailed case history, including production curves, of a flood in California (Ustick & Hillhouse, 1967). More recently, and also for a California reservoir, Tinker et al (1976) described field tests with two polymers to assess the effectiveness of each in reducing mobility.

Of particular interest to the writer are reports of Canada's first polymer flood in southern Alberta. In the initial paper on this project, Lozanski & Martin (1970) concluded that the polymer flood in Taber South was "economically successful". However, in a later report, Shaw & Stright (1977) discuss the difficulty of distinguishing the benefit produced by the polymer above that by water alone, and are unable to make any conclusion regarding the success of the polymer flood.

3.6 Recent Studies to Determine Field Performance

Recent laboratory work has concentrated on fundamental aspects of the flow and on refinements of the flood technique. Articles on the former are reviewed elsewhere in this report, and hence this section deals with applications-oriented research designed to aid the field unit.

Szabo (1975) used a carbon-tagging technique to investigate a number of factors related to flood performance, principally the slug size and the polymer concentration in it. By C-14 tagging polyacrylamide (PAM) molecules, he found that in low-permeability sands small amounts of polymer were effective in reducing mobility because of high polymer retention, and that the converse

was true in high permeability sands. While the tagging technique gives reliable mass measurements, Szabo did not check whether the tagging had any effect on the rheological and adsorption properties of PAM, i.e. do tagged and untagged PAMs behave the same way?

The simulation of field conditions in laboratory core samples was the concern in studies by Batycky (1981) and Schneider & Owens (1982). Batycky points out that laboratory cores must contain the same oil/water proportions as the reservoir, and that salinities of the experimental fluids must match those of the injected and connate water. He suggests techniques to meet these conditions. In a related study, Schneider & Owens tested PAM solutions in water-wet and oil-wet cores. Their main finding was that, in water-wet cores, polymer decreased the permeability to water significantly whereas the permeability to oil was not changed.

In their core tests, Scheider & Owens tried six different PAMs, but differences in flow resistance or retention were insignificant. Much more comprehensive evaluations were undertaken by Szabo (1979a,b) and Davison & Mentzer (1982). Szabo measured the viscosity-enhancement capabilities of 34 polymers - 12 different chemicals - over wide ranges in shear rate and salinity (1979a), as well as their adsorption and retention characteristics in porous media (1979b). From the viscosity data, Szabo does not make specific recommendations, but he does point out that biopolymers and partially hydrolysed PAMs (HPAMs) are stable in the long term when caustic is added and

that there are only minor differences among HPAMs. Following an analysis of his porous media data, Szabo gives two merit index rankings for the polymers, one ranking based on flow resistance, retention and cost, and the other based on retained properties after shearing.

Davison & Mentzer tested even more polymers, 140 in all, in an effort to find candidates for use in North Sea reservoirs. Their main concern was the performance of polymers in seawater and under reservoir conditions of high temperature, pressure and salinity. The 140 polymers were PAMs, polyvinylpyrrolidones, hydroxyethycelloloses, cellulose sulfate esters, guar gums, xanthans, and scheleroglucans. Comparisons, made by category and not by individual polymer, show that scheleroglucans are preferred for North Sea applications because they retain high viscosities over long periods of time, up to 500 days.

3.7 Reservoir Simulations

With high speed computers available for extensive calculations, one method of predicting polymer performance in the field is by mathematical simulation. To use this technique, core characteristics must be well known, as well as solution and surface properties of the polymer. By the use of finite difference techniques, one can predict the movement of a polymer slug through a reservoir and so estimate the recovery of oil. A good example of this technique is described in a paper by Vela et al (1976), who predicted incremental oil recovery for a reservoir

with vertically variable permeability. No comparisons are made with actual data; rather the model was used to compare production amounts with different injection programs.

4. POLYACRYLAMIDES

The principal polymer used in oil recovery, polyacrylamide, has been introduced in a prior report. Part B deals with dynamical properties of long chain polymers, and Section 2.1.1 therein describes the molecular structure of polyacrylamide (PAM) and discusses the practical relevance of parameters such as molecular weight and degree of hydrolysis. The shear viscosity of a polymer solution is its most important flow property, and Section 2.1.1 describes in detail how the shear viscosity of dilute PAM solutions depend on shear rate, on the concentration, molecular weight and degree of hydrolysis of the polymer, on the type and pH of solvent, and on the concentration of ions in solution.

Because the general properties of PAM solutions are well described in Part B, this section will concentrate on additional properties, particularly those that relate to oil recovery or flow in porous media. Friebe (1976) has made extensive measurements of PAM solution viscosity (which are described in Part B), but of more interest here are his studies of age and pH. His data show a significant drop in viscosity of a very dilute (30 ppm) solution over a period of 50 days, but an almost unchanged viscosity for a concentrated (1.5%) solution. Since the same histories were found for changes in pH, the observed decrease in viscosity is apparently due to a long term chemical interaction between the polymer and solvent.

Friebe also provides instructions on the preparation of PAM solutions. Such guidance must have seemed necessary at the time because Foshee et al (1976) published a paper in the same year on techniques of preparing and testing PAM solutions. Because the latter paper is in English and is so comprehensive - it covers topics like polymer storage, concentration measurement, thermal stability, microgels, and core sample artifacts - it is much more helpful. It is virtually a user's guidebook for handling PAM solutions.

Two other papers that provide guidance regarding the handling and testing of PAM solutions are by Knight (1973) and Shyluk (1975). Knight was primarily concerned with the effect of oxygen on solution stability, and hence studied how solution degradation depends on dissolved oxygen and on oxygen inhibitors. Degradation was monitored by the 'screen factor', the ratio of the pressure drop across a screen for a polymer solution to that for water at the same flow rate. Knight's results show that the screen factor was reduced by up to 30% when oxygen was present, and that sodium hydrosulfate and formaldehyde were effective in inhibiting this type of degradation. The effectiveness of formaldehyde was confirmed by field studies at two sites. Knight also looked at the effects of temperature and salinity on degradation and found that temperatures up to 140^{o}F and NaCl concentrations up to 2% did not appreciably alter the stability of the solutions.

Shyluk used the same parameter, the screen factor, to assess the ability of a particular PAM (Dow's Pusher 700) to reduce

water mobility. To avoid possible mechanical degradation, the flow rate through the screen was kept constant at a sufficiently low level. Shyluk tested a number of parameters, but mainly concentrated on effects due to salts, varying the type and amount. Consistent with other results, e.g. Durst et al (1981), he found that any salt decreased the screen factor of the solution. He also found that pH decreased the screen factor, as Friebe (1976) found, and that the screen factor is unchanged when nitrogen replaces the ambient air, a finding which seems to be at odds with other reports, e.g. Foshee et al (1976). Shyluk acknowledges that screen factor is not a good measure of polymer performance when mobility is partly due to adsorption; hence he attempts a return to tests with core samples, but does not really succeed in obtaining useful results.

Several minor papers should be noted before turning to the work of Chauveteau. Perhaps the most interesting of these is a claim that PAM is not a linear but a branched polymer. The statement, made by Ferrer (1973), was based on micrographs of evaporated solution droplets. Since his findings are not consistent with well-established molecular properties of PAM, it is strongly suspected that the branches are an artifact of his evaporation process. The other minor papers all deal with microgels in PAM solutions, a topic generated by Burcik. In a series of papers (Burcik & Walrond, 1968; Burcik, 1969; Burcik & Thakur, 1974), he argues that only aggregates of PAM molecules can explain porous media data, particularly the resistance due to viscoelasticity. But Lynch & MacWilliams (1969) refute the

arguments, and seriously damage Burcik's case by a correct calculation of molecular size. However, they are not able to settle conclusively the question as to whether microgels exist or not.

As suggested earlier, the most significant fundamental work on the flow of PAM solutions through porous media is by Chauveteau (1981) at the Institut Francais du Pétrole. His paper is concerned with adsorption (which will be dealt with in that Chapter), with shear and extensional flow effects in porous media, and how those effects depend on polymer concentration, solvent salinity, pore geometry and pore size. Flow data are plotted in a way which greatly helps to distinguish the various effects, viz: data of pressure drop versus flow rate for a porous medium are presented as apparent viscosity versus average shear rate at the wall; on the same graph are data of shear viscosity versus shear rate, as determined by measurements in capillary viscometers. The two sets of data coincide exactly when flow resistance in the porous medium is due to shear viscosity only, and a separation indicates an additional mechanism is operative. For example, when extensional flow ('dilatant') effects occur at high flow rates, the apparent viscosity is above the shear viscosity data and the point of departure is distinct. Chauveteau's graphs thus clearly indicate how onset of 'dilitancy' depends on polymer concentration, salt concentration and pore geometry. (Adsorption, equally well identified by this format, is left to Chapter 7.) Chauveteau tested a variety of porous media (filters, sandstones, packed beds), but the

essential test sections for his onset studies were single and multiple channel constrictions. His onset data seem to be well correlated by molecular parameters, but secondary flow was likely present in his case, and a more thorough study on molecular variables has been carried out by Durst et al (1981). Hence Chauveteau's valuable contribution is a format which clearly distinguishes between adsorption, shear viscosity and extensional viscosity in porous media flow.

5. POLYSACCHARIDES

While polyacrylamide has been used in almost all polymer floods, there is growing interest in the use of biological polymers, particularly polysaccharides. These polymers are equally effective in increasing the shear viscosity but they are much less susceptible to mechanical degradation. Current industrial research seems to focus on the rheological characterization of polysaccharide solutions and on their flow through porous media.

An introduction to polysaccharides and to the rheology of polysaccharide solutions was presented in Section 2.1.3 of Part B. The key point from that description is that the molecular structure of these polymers is a helial coil, quite unlike the random coil of PAMs (see also Wellington, 1981). Polysaccharide molecules therefore behave as long rubbery rods and the rheology of a solution is similar to that for suspension of long particles. Fundamental research on the rheology, and on flow through porous media, has mainly come from Chauveteau and co-workers at the Institut Francais du Pétrole, judging by information available in the open literature. In his articles, Chauveteau superposes porous media data and shear viscosity data similar to the format used for polyacrylamide solutions; that is, the rheological data of shear viscosity versus shear rate are superposed on porous media data of apparent viscosity versus shear rate. Results are presented in this fashion for a variety of porous media (Chauveteau & Zaitoun, 1981, and Chauveteau,

1982) and the graphs appear to be very similar to those for PAM solutions: (i) the solutions are highly shear-thinning, (ii) at sufficiently high shear rates, the apparent viscosity becomes higher than the shear viscosity because of extensional flow effects, and (iii) as pore size becomes smaller, the apparent viscosity decreases. In the case of PAM solutions, this latter effect is mainly due to absorption, but in the case of polysaccharide solutions, the effect is due to a depleted layer near the wall. That is, the centre of a rodlike molecule can generally be no closer to the wall than half the rod length. Hence, with few molecules near the wall, there are more molecules in the region where dissipation is less and so the viscosity is lower. Chauveteau made predictions of reduced viscosity based on a molecule-free layer near the wall; when the layer was about half the known rod length, the predictions agreed well with experimental data. Chauveteau also shows how a layer of constant thickness explains reductions in apparent viscosity for packed beads and for porous media of irregularly-shaped particles.

Another aspect of polysaccharides which has concerned Chauveteau and others are the microgels which can form in aqueous solutions. These intermolecular aggregates can foul up laboratory tests and so were removed for the research described above. However, they are a fact of life in field tests and can cause plugging. Consequently, Chauveteau & Kohler (1980, 1981) conducted laboratory flow tests with microgels in the solutions. Basically, they showed that microgels act like extralarge

macromolecules and they indicated how to eliminate them or what to expect if they are used in reservoirs.

Another concern about polysaccharides is degradation, both shear and microbial. Tests, such as those done by Szabo (1979a), confirm that polysaccharides are resistant to shear, and recent work is trying to establish microbial effects (Brierly et al, 1981).

6. RHEOLOGICAL EFFECTS

6.1 Non-Newtonian Flow in Porous Media

The original idea in adding polymer to water flooding was to increase the viscosity of the water and so reduce its mobility in porous media. It has since become apparent that the polymer causes a variety of effects when it flows through porous media, and in this chapter we concentrate on the original effect and on another bulk property which increases flow resistance, the extensional viscosity.

First, to be clear on terms, shear viscosity is defined as the viscosity measured in shear flow, such as in a tube viscometer or a Couette viscometer. For Newtonian liquids, this property is the only flow property of the fluid and is independent of shear rate. For a non-Newtonian fluid, not only does the shear viscosity depend on shear rate, but additional flow properties are required to characterize the fluid. The most important of these for our purposes is extensional viscosity, the resistance to purely extensional motion. This property is defined and discussed in Section 2.2 of Part B. It should be noted that the extensional viscosity is exactly three times the shear viscosity for a Newtonian fluid, and that the factor may be as high as $O(10^3)$ for polymer solutions.

It should also be noted that the term extensional viscosity is fairly recent. The former term, viscoelasticity, which appears throughout the porous media literature, has been dropped

for two reasons. One, viscoelasticity has been used to describe the response of a fluid to small-amplitude oscillatory shear flow. Secondly, a liquid did not have to be elastic to produce extensional flow effects, i.e., suspensions of long particles (rods or threads) can produce high values of extensional viscosity and these fluids do not exhibit elastic recoil. Another synonymous term in the porous media literature is dilatancy. In rheology, the strict meaning of this term is that shear viscosity increases with shear rate. When extensional flow effects were first observed in porous media, they were thought to be due to shear and hence the use of the term. However, even though 'dilatancy' is now known to be an effect of extensional viscosity, the term persists, principally favoured by petroleum engineers.

In the first section of this Chapter, the relation between porous media flow and shear viscosity is discussed. The second section treats extensional viscosity effects in the same media, and the last section looks at the same effects in other small channels.

6.2 Effects Due to Shear Viscosity

As noted in Section 3.3, the first laboratory studies on the flow of polymer solutions through porous media were reported by Sandiford (1964) and Pye (1964) in back-to-back articles in the Transactions of the Society of Petroleum Engineers. Both tested solutions of hydrolyzed polyacrylamide (HPAM) in sandstones, but

Pye's format demonstrated that the flow resistance was larger than that due to viscosity alone.

Rheological studies followed shortly thereafter. In the first ones, by Sadowski & Bird (1965) and Sadowski (1965), a variety of mildly concentrated solutions were pushed through beds of packed beads. The shear viscosity of these fluids was also measured and the data fitted by the Ellis model. Then the Blake-Kozeny equation (for Newtonian fluids in porous media) was modified to describe Ellis model fluids. Data from the packed bead experiments were well correlated by the modified equation, except for the highest molecular weight polymer at the highest flow rates. Sadowski and Bird show that adsorption could not have played a role in the experiments and interpreted the somewhat higher resistance at high flow rates as an effect due fluid elasticity.

Remarkably, four papers then followed which tried to prove that Sadowski & Bird were wrong, viz., that elastic effects do not occur in porous media flow. The chief protagonist was Middleman (Middleman & Christopher, 1965, and Middleman & Giatonde, 1967), with support from McKinley et al (1966) and Kozicki et al (1967). All four papers describe experiments on porous media flow and all four found "no evidence of viscoelastic effects". The issue was conclusively settled by two papers which appeared in August, 1967. Marshall & Metzner (1967) demonstrated that viscoelastic effects could increase the pressure drop by factors as high as O(10) and also showed that adsorption could not be the cause. Dauben & Menzie (1967) tested dilute to

semi-dilute solutions of polyethylene oxide (PEO) in beds of fine beads, and measured 'apparent' viscosities up to 30 times a fluid's shear viscosity. Even though PEO is not used in the field, Dauben & Menzie's paper must be considered be a landmark. It was the first paper to use solutions in the relevant concentration range, i.e., dilute to semi-dilute, and it was the first to vary concentration, molecular weight, flow rate, and bead size. Viscoelastic effects were found to increase with the first three and decrease for the last one.

We are actually getting ahead of ourselves since viscoelastic effects (extensional flow effects) are to be covered in the next section. It is important to realize, however, when researchers first separated viscous and elastic effects. A great deal of research on viscoelasticity followed, for this topic was of considerable interest to the rheology community.

However, it was realized that flow rates in underground reservoirs are generally too slow to induce elastic effects and thus a number of researchers continued to focus on inelastic non-Newtonian behaviour in porous media. Slattery (1967), for instance, modified Darcy's law for two non-Newtonian fluids, the Ellis model and the Noll simple fluid. However, the fluid model usually adopted for non-Newtonian fluids is the simple power-law model, and a number of authors derived relations analogous to Darcy's law for this fluid: White (1968), Wissler (1971), Kozicki et al (1972), Odeh & Yang (1979) and Kumar et al (1981). These papers present analyses which are generally more complex than the earlier analyses with the some model, i.e. those by

Christopher & Middleman (1965), Giatonde & Middleman (1967), Marshall & Metzner (1967), and Kozicki et al (1967), but the results seem to be about the same. Perhaps the most comprehensive of these works is that by Kumar et al because they correlate, rather successfully, most of the available experimental data. It should be noted that almost all the solutions for which experimental data have been obtained have been concentrated solutions, generally much above the dilute to semi-dilute range applicable to polymer flooding. It should also be noted that the power-law model describes only a portion of viscosity versus shear rate curve for polymer solutions. As shown by the figure on page 9 of Part B, there are constant-viscosity plateaus at very low and very high rates of shear, and so the power-law model is valid only in the intervening shear-thinning region. A more realistic model should incorporate the low shear plateau (the high shear plateau can be neglected because elastic effects will then dominate in porous media flow) and efforts have been made in this vein: for example, the Ellis model by Sadowski & Bird (1965), Slattery (1967), Kozicki et al (1967), and more recently the Carreau model by Chauveteau and colleagues. These more refined models have an extra parameter which improves fits to data, but it is not clear that the refinement is necessary. As noted, Kumar et al (1981) achieved a comprehensive correlation of data with the power-law model, and Christopher & Middleman (1965) fitted Sadowski's (1965) data by a power-law model as well as Sadowski did by the Ellis model.

6.3 Effects Due to Extensional Viscosity

The previous section described the finding that elastic effects appear in porous media flow when the flow rate is sufficiently high. The research which followed dealt mainly with PEO solutions, mainly because this polymer is neutral and therefore simplifies experiments, and because dilute solutions exhibit very large extensional flow effects.

The first group to work with dilute solution were Dauben & Menzie (1967), for their concentrations of Polyox Coagulant extended down to 250 ppm. They were primarily interested, however, in the semi-dilute regime where their PEO solutions were characterized by power-law parameters. Jones & Maddock (1966, 1969) measured pressure drop with dilute solutions, but they were interested in the onset of elastic effects and consequently they did not explore the possible magnitudes of viscoelastic effects. The first group to do so, and with truly dilute solutions, were James & McLaren (1975). Their solutions were as dilute as 6 ppm, and their data show this amount of polymer could increase the pressure drop across a packed bead by a factor of ten. They systematically varied bead size, polymer concentration and molecular weight, and showed that the onset of viscoelasticity is related to the kinematics of the flow, i.e., for a particular solution but different porous media, onset occurred at a particular deformation rate. James & McLaren also conducted flow visualization studies and confirmed that there was no secondary flow in the cavities. Similar studies with dilute PEO solutions

were made by groups at Universität Karlsruhe: Naudascher & Killen (1977) and Käser & Keller (1980). The first paper focussed on onset conditions and showed that onset was correlated by the product of the deformation rate, the first Rouse relaxation time (Sec. 3.2 of Part B) and the square root of the concentration. The last parameter makes the product dimensional and was included in an ad hoc manner to collapse the data. The second paper is a thorough investigation of PEO degradation in porous media, a much needed study because PEO is known to degrade easily. The results show that degradation increased with velocity and decreased with bead size, confirming the intuition that degradation increases with deformation rate. Rath & Sarat (1977) also measured the resistance of PEO solutions, but concentrated on permeability. Their media were beds of glass beads, and they determined the change in permeability to both water and kerosene flow.

Although PEO is easy to work with in the laboratory, it degrades too easily in enhanced oil recovery and hence PAM is generally used. It appears that extensional flow effects with PAM have been studied by only two groups: Durst and his colleagues at Karlsruhe and Chauveteau and co-workers at the Institut Francais du Pétrole. The most extensive work is by the Karlsruhe group, for they varied the flow rate, bead size, molecular weight, concentration, degree of hydrolysis, temperature, and the number and type of ions in solution (Durst et al, 1979, 1981, 1982a,b; Durst & Haas, 1981, Haas & Durst, 1982, and Interthal et al, 1981). They were able to correlate

their extensive data by two dimensionless groups based on the FENE model for flexible macromolecules. That model, the best one available, is described in detail in Section 3.4 of Part B. In essence, all the molecular parameters varied by Durst et al are grouped in the first Rouse relaxation time (Sec. 3.2 of Part B) and their onset data are correlated by the product of this time and the deformation rate. While the correlation is very good overall, it is not fully satisfactory because it does not completely correlate concentration and molecular weight, the two most difficult parameters. Durst and company also appear to correlate the magnitude of extensional flow effects, but the correlation is really dependent on a free parameter from the FENE model.

In Chauveteau's studies (1981), onset was found to be correlated by the product of the deformation rate and the first relaxation time, similar to Durst, but the correlation is over a much wider 60-fold variation in concentration. However, Chauveteau's onset data are not for porous media but for suddenly contracting flows in which secondary flow was likely present.

There have been several studies of such entrance flows, but before proceeding to them, it should be noted that there has been one theoretical study of dilute solutions in porous media. Daoudi (1975, 1976) solved the deformation of a randomly-coiled macromolecule flowing through a periodically-constricting channel and found the consequent energy dissipation. The analysis was undertaken to explain the peaks in viscoelastic effects found by

James & McLaren (1975), and Daoudi was able to produce curves which were qualitatively very similar to the experimental curves.

6.4 Extensional Viscosity Effects in Converging Flows

As stated in the previous section, entrance or converging flows of dilute solutions have been investigated primarily to understand extensional flow effects in porous media. Non-Newtonian effects at the entrance to tubes have been studied by measuring changes in the velocity field and entrance pressure loss. For solutions of nonionic and anionic PAM in the 100 ppm range and above, it was found that the entrance pressure increases suddenly at a particular flow rate and the entrance flow simultaneously contracts (Chauveteau, 1981; Chauveteau et al, 1978; and Hoa et al, 1982). It was also found that the extra pressure increases with shear rate to the power 1.6 (Moan et al, 1979) or 2 (Ghoniem, 1979). This finding is somewhat at variance with the more recent work of Fruman & Barigah (1982), in which the relation was almost perfectly linear. The discrepancy may partly be explained by the fact that the solutions of Fruman & Barigah were much more dilute, 100 ppm being their maximum concentration.

The studies of James & Saringer (1980, 1982a, 1982b) were also in the very dilute regime, for their primary test fluid was a 20 ppm solution of PEO. Their experiments with axisymmetric channels of various shapes showed that significant extensional flow effects were possible without a change in the flow field,

and that these effects did not appear in planar flows at the same rates of deformation.

All these converging flow studies show effects similar to those in a porous medium, that is, extensional viscosity effects can significantly increase pressure loss, and onset is governed by a critical deformation rate in the flow.

7. ADSORPTION

7.1 Introduction

As explained in Chapter 1, adsorption is one of two basic mechanisms by which polymers change water mobility in porous media. Many studies of mobility control deal with both adsorption and increased fluid viscosity, but in this chapter we will attempt to cover research papers that deal primarily with the former.

The chapter is organized into three sections. The first deals with fundamental experiments on adsorption, going back to Rowland & Eirich's benchmark work in the mid 1960s. The next section deals with the polymers and adsorbing surfaces of direct interest to enhanced oil recovery, i.e. principally polyacrylamide (PAM) in contact with natural or synthetic porous media. The last section covers adsorption theories which attempt to predict the properties of adsorbed macromolecules from polymer and solvent properties.

7.2 Fundamental Research

References in recent papers on adsorption generally go back to the work of Rowland & Eirich and co-workers (1965, 1966a and 1966b). They determined the thickness of an adsorbed polymer layer by measuring increased resistance in tube flow, and equating the increase to an effective decrease in tube diameter.

By testing a variety of polymers in various solvents, they found that the effective film thickness, L_H, was about the same thickness as the free coil diameter; that is, L_H is about 2 R_G, where R_G is the radius of gyration of the macromolecule. From these results, they reasoned that the polymer adsorbed as a monolayer, was in a highly extended configuration overall but had a higher density of segments close to the wall.

Harrington & Zimm (1968) extended this line of research by investigating glass disks with very fine pores. Not surprisingly, they found that plugging occurred when the macromolecular coils were of the same order as the pore size. But, with lower molecular weight samples, adsorption data agreed with those of Rowland & Eirich.

The tests described above were all done with neutral polymers. One of the first studies with a polyelectrolyte was by Greene (1971), who examined the adsorption statics and kinetics of sodium polydisulfoethylmethacrylate. For a fixed molecular weight, he found that the amount of adsorption increased significantly as the concentration of salt in the solvent increased. Under the same conditions, viscometric tests showed that the size of molecular coils decreased. Despite this apparently conflicting behaviour, calculations of L_H based on a monolayer thickness still yielded the usual values of about 2 R_G.

Gramain (1975) and Pefferkorn et al (1978) tried to correlate adsorption data with the intrinsic viscosity [η] of the

polymer. For polyvinyl acetate adsorbed on cellulose filters, Gramain found that L_H was proportional to $[\eta]$, but Pefferkorn et al tried a different polymer-solvent system and L_H was linear with, but not proportional to, $[\eta]$. This latter relation was also obtained by Dejardin & Varoqui (1981). Hence the form of the L_H-$[\eta]$ relation is not yet clear. In addition to their experiments, Dejardin & Varoqui developed a theory which coincided with their data and this theory will be discussed in Section 7.4.

7.3 Research Related to Oil Recovery

In the 1960s, there was some confusion regarding the role of adsorption in reduced mobility. Hence reserach papers from that period tried to clarify how permeability is lowered by adsorbed polymer and a good example is the paper by Gogarty (1967). Another early paper which singled out adsorption effects was by Desrémaux et al (1971). That group concentrated on the absorption characteristics of PAM and polyethylene oxide (PEO), generally dissolved in a 2% NcAl solution, and compared amounts of adsorption on a variety of stones and minerals. It is perhaps surprising to see PEO as a polymer of interest, but its well-known susceptibility to flow degradation was probably not recognized at that time.

The polymers of prime interest, PAM and polysaccharide, were tested for adsorption on glass by Thomas (1976). For PAM, he concluded that the thickness of the absorbed layer was about the

molecular diameter and that the thickness was not changed significantly by the flow rate. More interestingly, he showed how the addition of cations can develop cross-links and how repeated applications can build up an adsorbed layer many times thicker than a single-pass monolayer. Sparlin (1976) also measured the adsorption of PAM, and he tested a variety of commercial samples on a number of natural media, with and without salt in the water. The results from his extensive program provide useful guidelines for matching polymer to media for successful field treatments. For example, one of his eight conclusions is that anionic PAM is more effective on carbonates than on sand. Sparlin also shows that saline decreases the film thickness, a finding consistent with Greene's (1971) results with another polyelectrolyte.

The adsorption behaviour of PAM was also investigated by Hollander et al (1981). They selected a single test substrate and chose sodium kaolinite because it is the surface-active constituent of reservoir media like Berea sandstone. From kinetic tests, they found that maximum adsorption was reached in about 15 minutes, quite in contrast to the 10 days observed by Gramain (1975) for polyvinyl acetate in cellulose. Hollander also compared nonionic PAM with an ionic copolymer. For the former, the intrinsic viscosity and the amount of adsorption were independent of the ions in solution, as one might expect. For the latter, $[\eta]$ decreased and the amount of adsorption increased as the ionic strength increased. The latter facts seems contradictory, but the ions shield the charges along the chain

and thereby permit the molecule to approach the surface and bond with complementary groups on the surface.

As already mentioned in Chapter 4, Chauveteau and co-workers at the Institut Francais du Pétrole have extensively investigated PAM adsorption on porous media (Chauveteau & Moulu, 1978; and Chauveteau, 1981). Their articles describe calculations of adsorbed layer thickness inside a porous medium, based on a method similar to that developed for a cylindrical channel. Based on this method, experimental values for L_H turn out to be the same as those for simpler surfaces, viz., L_H is slightly higher than 2 R_G. Their results also show that (i) there is a depleted layer above the adsorbed layer, a steric exclusion effect as discussed in Section 8.2.3, and (ii) L_H appears to increase with flow rate.

The cause of this latter effect is not discussed by Chauveteau, but is part of some interesting research by Gramain & Myard (1981a,b). They tested partially hydrolyzed polyacrylamides (HPAM) in Millipore filters with cylindrical pores, and applied the usual Poiseuille formula to find L_H and measured the amount adsorbed by spectroscopic methods. They found that the amount adsorbed was independent of pore radius, was independent of molecular weight for $M_w > 10^6$, and reached a maximum in 72 hours for a 100 ppm solution (cf. 15 minutes for a 1500 ppm solution, as reported by Hollander et al, 1981). Their data also reveal how L_H increases with concentration, with M_w (L_H is slightly greater than 2 R_G) with pH, and, most surprisingly, with velocity. Their latter paper (1981b) treats

the last effect separately, showing how L_H suddenly increases by as much as six times once the velocity is above a critical value. They attribute the effect to coil-stretch transition of the free loops and consequent larger hydrodynamic forces. This explanation is credible except that data from different-size channels are correlated by mean channel velocity and not by a velocity gradient. Another possible explanation are extensional flow effects at the entrance to the channel (Section 6.4), but these too should be correlated by a velocity gradient and not by velocity. Hence, the interesting observations of Gramain & Myard remains unexplained.

One other paper on PAM which should be mentioned in this section is the recent work by Baijal & Dey (1982). Their experiments with HPAMs repeat earlier work but they usefully show that adsorption was a maximum when the degree of hydrolysis was about 30%.

As for other polymers, very little work has been done. Jones & Ho (1979) tried to show that the PEO data by James & McLaren (1975) could be explained by adsorption, but this conflicts with latters' permeability measurements before and after the polymer solution runs. We have already mentioned that Desrémaux et al (1971) conducted tests with PEO, but we did not mention the results: PEO absorbs much better than PAM and salt promotes adsorption. An alternate polymer of true interest is of course polysaccharide, which is thought to be non-adsorbing. That is not the case, apparently, for Duda et al (1981) measured the adsorption of Xanthan on sandstones, and learned that (i) the

calculated absorbed layer has an effective thickness which is a fraction of the length of the molecule, and (ii) the permeability of the medium, with Xanthan absorbed on the surface, increases with shear rate. This behaviour is opposite to that observed for PAM, but is more physically reasonable. That is, the rods are likely attached at one end and, at high flow rates, the large hydrodynamic forces deflect the rods so they offer less resistance to the flow. This mechanism should make itself evident by an onset shear rate, but unfortunately, the data are not plotted so that onset behaviour can be detected.

7.4 Theoretical Work

A number of theoretical papers dealing with adsorption have appeared in the literature, and most of these are by physical chemists concerned with chain statistics, molecular configuration, and so on. The only exception is a paper by Hirasaki & Pope (1974) who treat bulk rheological effects, shear-thinning and dilatancy, as well as adsorption. A few comparisons are made with experiments, but the overall impression from the paper is that the authors' predictions are speculative.

As for the work done by chemists, a good introductory article on molecular theory and experimental technique is one by Ash (1973). Specific theories for adsorbed polymers have been developed by groups at the National Bureau of Standards, the Centre de Recherches sur les Macromolecules in Strasbourg, and by the Laboratory for Physical and Colloid Chemistry in Wageningen,

Holland. The first group, Dimarzio & Rubin (1978), adapted the classical bead-spring model of Rouse to adsorption by considering the molecule to be attached at one point to a wall over which the flow is simple shear. Actually, they first considered a single bead at the end of a tethered spring and then generalized to an N-bead molecule. They found that the energy dissipated by an N-bead molecule is exactly twice that of a freely-convected molecule at the same shear rate, which makes physical sense. Unfortunately, their analysis shows that polymer segments of the attached molecule undergo internal circulation, just as for a free molecule. How this internal circulation proceeds, when one point of the molecule is fixed, is rather difficult to imagine.

The second group is Dejardin & Varoqui (1978). They applied the low-Reynolds-number field equations to the adsorbed layer, assuming bead drag for the polymer segments and assuming an exponential distribution of segments away from the wall, analagous to the exponential distribution in a random coil. Their analysis leads to the prediction that L_H is a linear function of $[\eta]$, consistent with experimental results by them and Pefferkorn et al (1978), as mentioned in Section 7.2.

Another approach to the molecular theory of adsorbed chains have been made by deGennes (1976) using his polymer scaling theory, and by Scheutjens & Fleer (1979, 1980, 1982), who used a lattice model to simulate configurations. These theories pay a good deal of attention to physics at the molecular level but provide little that is useful for engineering applications.

In summary, a proper theoretical framework is still required for dealing with hydrodynamic effects caused by adsorbed polymer chains. Almost by direct analogy, the theory appears to be at the same level as that for convected macromolecules in a high shear flow.

8. OTHER POLYMER EFFECTS IN POROUS MEDIA

8.1 Experimental Findings

While the main effects of polymer in porous media flow are thicknening and adsorption, additional effects are produced and they will be described in this chapter. Although they are treated here as separate effects, it will soon be apparent that the mechanisms are related.

8.1.1 Hydrodynamic Retention

The first effect is termed hydrodynamic retention to distinguish it from adsorption or chemical retention. This phenomenon was first described by Maerker (1973). He monitored the flow resistance and effluent concentration for PAM and polysaccharide solutions in a sandstone, and noted the transient response when a previously steady flow was stopped for 16 hours and then resumed at the same pressure drop. He observed that the effluent concentration first increased sharply from its steady-state value (equal to the inlet concentration) and then dropped slowly down, sinking below the steady-state level before climbing back to it. An identical pattern was followed by the flow resistance (mobility reduction), and similar results were observed where the pressure drop across the core was suddenly increased without stopping the flow. These observations were interpreted by Maerker and later researchers in the following

way. Because of some undefined hydrodynamic force, the molecules migrate to stagnant zones or become trapped in small cavities. When the flow stops, these molecules diffuse into the larger cavities, so that when the flow starts again, they cause a larger viscous resistance and then are flushed from the system. Hence the flow resistance and effluent concentration are initially larger. During the new steady flow, hydrodynamic forces again cause molecules to be 'stored' in the medium and equilibrium is restored. Chauveteau & Kohler (1974) reported similar results, but they add confusion by showing other stop-start data in which the effluent concentration remained constant. The flow resistance dropped sharply after the step change.

In both experiments, polymer adsorption occurred simultaneously. While adsorption is generally independent of flow rate (see Thomas, 1976, and Section 7.3), it is not clear if that was the case here and it is not clear whether adsorption and hydrodynamic retention are independent of each other.

8.1.2 Mechanical Entrapment

A clever experiment which got around the adsorption problem was conducted by Dominguez & Willhite (1977), and it revealed a similar but different retention mechanism. They used a non-adsorbing porous medium — compacted Teflon powder — and experimentally verified that adsorption was negligble. Slugs of polymer solution, typically several pore volumes, were injected between brine flows and, from measurements of polymer

concentration in the effluent, the amount retained by the medium was detected. The amounts were typically 20 µg per gram of medium, the same order as the amounts for adsorption, and these increased with bulk concentration and flow rate. Because the residual resistance of the medium was found to be higher by factors of 1.5 to 3.0, they reasoned that the polymer was trapped in the smallest passages. However, they did not test the permanency of the changed resistance by retesting at a later time, say 16 hours later to be comparable with Maerker. Hence mechanical entrapment may be just the short-time manifestation of hydrodynamic retention, but their experiments at least make it clear that the mechanism can change permeability over short time periods.

Szabo (1975) also measured 'permanent' changes in permeability and, by a carbon-tagging technique, was able to distinguish between adsorption and flow-caused retention. Like Dominquez & Willhite, Szabo cannot say anything about the permanancy of the changes but he does add some other useful information: (i) his tagging technique shows that polymer retention decreased rapidly with distance into his sand packs, consistent with the idea that the largest molecules in the solution are trapped at the beginning, (ii) adsorption is the dominant retention mechanism for medium-permeability pores and entrapment is dominant for low-permeability pores; this too is consistent with the idea of large molecules plugging small pores.

8.1.3 Inaccessible Pore Volume

Another interaction between polymer and porous medium has been proposed because of yet another experiment. Dawson & Lantz (1972) measured the speed of propagation of a polymer slug in a porous medium, and then measured the speed of salt under the same conditions. The former propagated more rapidly, apparently because the macromolecules bypassed pores which were too small to enter. This portion of the medium which the polymer could not enter has been termed "inaccessible pore volume", and the data of Dawson & Lantz' indicate that it constituted about 30% of the pore volume. In his carbon-tagging experiments, Szabo (1975) compared tracer and polymer speeds and determined that about 22% of his pore volume was not accessible to polymer flow. It is clear that this size exclusion mechanism is the same one operative in gel permeation chromotography (GPC), the well known analytical tool for separating molecules of different size in order to determine the molecular weight distribution of a polymer sample. What is less clear is how this mechanism is related to the previous two, because size exclusion effects can certainly take place without any polymer retained by the medium, as in GPC. Dawson & Lantz do not shed any light on this problem because physical adsorption also took place in their work. But, in Szabo's work, the polymer was definitely trapped in the medium, suggesting that inaccessible pore volume and mechanical entrapment are the same thing. Willhite & Dominguez (1977) have written a review article about all three mechanisms, but they

were more interested in description than analysis, and do not attempt to connect the mechanisms.

The only truly scientific work related to these phenomena was carried out by Aubert & Tirrell (1980a). They studied retention with polymers having narrow molecular weight distributions (polystyrene) and with non-adsorbing porous media having variable but well-defined geometries (GPC columns). By making step changes in the flow rate and measuring the consequent changes in effluent concentration, they determined that (1) polymer is retained in the micropores of the columns, not in the relatively stagnant zones, (2) retention increases with flow rate, and (3) retention increases with molecular weight, until the molecules are too big to enter a micropore. These results suggest that hydrodynamic retention and mechanical entrapment are the same mechanism. With more well-conceived experiments like that of Aubert & Tirrell, it should become clearer what the relation is among the three mechanisms.

8.2 Theories on Polymer-Pore Interactions

The experimental work described in the previous section has generated some theoretical work to explain the phenomena. Most of the work has been concerned with flow induced diffusion of macromolecules, but trapped polymer chains have also been examined, and we include here theoretical work on steric exclusion. This latter topic is admittedly only marginally related to size exclusion effects, but it is included here

because it is a polymer-medium interaction and because the analyses are similar to the other theoretical work.

8.2.1 Flow-Induced Diffusion

There have been two schools of research on this topic, one led by Metzner and the other by Tirrell. Metzner's approach has been mainly macroscopic and based on thermodynamic arguments (Metzner et al, 1978; Janssen & Metzner, 1980; Janssen, 1980). Based on an elastic-dumbell analysis by Marucci (1972), Metzner predicted a diffusion of macromolecules toward zones of low stress and consequent changes in concentration. He and co-workers have attempted to explain a variety of phenomena by this diffusion – e.g., 'slip' in capillary flow, retention in porous media and blood flow – but their analyses and experiments do not yet seem convincing (more results are promised).

Tirrell & Malone (1977) investigated the effect of stress on macromolecular diffusion by considering the dynamics of an N-element bead-spring model and predicted that migration depends on a variation of shear rate. Later Aubert & Tirrell (1980b) generalized the work to non-rectilinear flows and showed that molecules migrate to regions of highest streamline curvature. In porous media flow, the regions of highest curvature are close to the wall, and hence Aubert & Tirrell can explain how molecules were driven into the micropores in their GPC experiments (Aubert & Tirrell, 1980a).

A similar bead spring analysis has been carried by Shafer and colleagues (Schafer et al, 1974; Shafer, 1974). They were primarily interested in the migration of DNA molecules in circular Couette flow and its possible application to size separation. The analysis predicts that migration proceeds toward the inner wall, where the shear stress and curvature are highest, and that the rate depends on the 5/2 power of the molecular weight. However, no experiments have been carried out to check their theory.

8.2.2 Dynamics of Confined Macromolecules

Professor deGennes and co-workers at the College de France have examined the dynamics of polymer chains trapped in pores, i.e., the pore cross-dimension is generally less than the diameter of a randomly-coiled chain. Daoud & deGennes (1977) studied statistical properties of confined chains using scaling theory, and provided qualitative estimates for parameters like molecular size and thermodynamic potential. Brochard (1977) continued this line of research by investigating the dynamics of the chains, including effects due to free volume and hydrodynamic interaction, and predicted the translational diffusion coefficient to within an arbitrary constant. In Brochard & deGennes (1977), some of these concepts are repeated and, more importantly for our purposes, the case of solvent flowing through a confined chain is studied. Specifically, they treat the case of solvent flow in a conical channel containing a chain, and

predict the flow rate and pressure difference necessary to lodge the chain in the channel. Interestingly, the required solvent flow is independent of molecular weight. However, like so much of the work in this area, no experiments were done to confirm the theory.

8.2.3 Steric Exclusion

As briefly described in Section 1.1, steric exclusion refers to the fact that the centre of mass of a macromolecule can be no closer to a wall than half its size, thereby leaving a layer depleted of molecules. In very small channels, this removes molecules from a region of high dissipation and hence the overall or apparent viscosity decreases (Chauveteau, 1979, 1982). Modern work on this problem was initiated by Brunn (1976), who assumed hard core repulsion between the wall and sphere-equivalent polymer segments and predicted an effective slip velocity, or decrease in apparent viscosity. (In an earlier work, Lifson (1956) predicted a viscosity increase). Aubert & Tirrell (1982) used the Rouse model without the artifice of hard core repulsion and predicted consequent reductions in viscosity. Their predictions agree surprisingly well with the data of Chauveteau when it is considered that the experiments were done with rodlike Xanthan and the theory is based on the randomly-coiled Rouse model. Actually, the problem of rigid rods was treated by Auvray (1981), who predicted a reduction in viscosity dependent on the square of the aspect ratio, but who did not compare his

predictions with the data of his colleague Chauveteau. Hence, while theory and experiment have not been matched completely, there is considerable activity in this area and good agreement will likely be achieved.

9. MECHANICAL DEGRADATION OF POLYACRYLAMIDE SOLUTIONS

The two major weaknesses of polyacrylamide for enhanced oil recovery are its viscosity loss in brine and its mechanical degradation. The change of viscosity with salt concentration has already been discussed in Chapter 4, and in this section, we examine what is known about the rupture of PAM chains due to hydrodynamic forces.

Polymer degradation can occur in any flow at sufficiently high flow rates, but for purposes of simplification, degradation is usually studied in simple shear flow or purely extensional flow. The more basic flow is the former, of course, but there does not appear to be any work on PAM degradation in this flow field. Ghoniem et al (1981) started such a study by using capillary tubes, but found that degradation was independent of tube length and realized that molecules were being ruptured in the converging flow at the tube entrance. The entrance pressure drop was larger than for the solvent because of extensional viscosity, and Ghoniem et al found that the relative change in this extra pressure drop was a function of the number of passes through a tube and, surprisingly, was independent of shear rate in the tube. It was observed that degradation started when the shear rate in the tube reached $1.1 \times 10^4\ s^{-1}$, but unfortunately, this value cannot be related to the more meaningful rate of extension in the entrance flow because the latter is not well enough defined.

The first study of PAM degradation in porous media was done by Maerker (1975). He detected degradation in a fluid by measuring change in its shear viscosity and screen factor (This latter parameter, described in Chapter 4, is the pressure drop across a particular screen at a fixed flow rate and is a sensitive measure of extensional viscosity). From data on various lengths of a sandstone, Maerker found that degradation increased with length, flow rate and salinity. He was able to correlate data for the first two effects by plotting per cent loss of screen factor against a new parameter, the product of dimensionless flow distance and extensional deformation rate. Maerker discusses the relevance of his experiments to field conditions, and demonstrates how severe degradation near the injection well can reduce polymer effectiveness by 80%.

In later papers, Maerker (1976) and Seright & Maerker (1981) included the effect of porosity in degradation tests and measured changes in the molecular weight distribution. Data in the latter paper show that the high molecular weight tail is attenuated by degradation, but the tails of high and low molecular weight samples were affected equally. Just as surprising, the peak of the distribution was not changed by degradation. These last results are contrary to the long-held idea that degradation most affects the largest molecules in solution.

Seright (1980) presented a new parameter to correlate degradation data, namely one which is effectively the strain rate divided by the grain diameter. By this parameter, he successfully collapses not only his own data but also the prior

data of Maerker (1975). Another group to challenge Maerker's correlation were Martin & Ward (1981). They found that Maerker's correlation parameter works well for cores of high permeability, but not for very low permeability cores. This finding is not surprising because, for small pores, inaccessible pore volume is likely a factor and the extensional rate (which is necessary for the correlation) is hard to estimate. However, when these size effects are accounted for, the data are shifted in the direction of the general correlation.

Two other works should be mentioned here for the sake of completeness. Batacky & Masata (1978) and Kilmer et al (1981) followed the prior work and detected degradation by screen flow measurements. The latter report is only preliminary and the first did not improve the writer's understanding of degradation.

In summary, the available research on degradation indicates that degradation can be a problem in porous media flow because of the extensional flow component. Experimental data have well established that degradation increases with flow rate and salinity and decreases with grain size. While the data confirm that it is extensional motion which causes degradation, there do not seem to be studies on degradation in well-defined extensional flow fields.

10. GEOMETRICAL MODELS OF POROUS MEDIA

One avenue of research on porous media flow has been the study of flow through a single channel whose shape produces a flow history similar to the sequence of squeezing motions in a porous medium. The basic flow pattern is therefore convergent-divergent flow, and a number of researchers have modelled a porous medium as a periodically-constricted tube, or as a bundle of such tubes. Most of the work has been done for Newtonian fluids. Solutions of the Newtonian problem provide the basis for non-Newtonian flow, of course, but they are also necessary to understand phenomena such as dispersion and heat transfer in porous media.

Perhaps the singular work in this area is Franzen's research on flow through regularly-spaced beads. This work differs from the remainder in this chapter in that it is experimental and involves spheres, but the model is probably the closest to a natural porous medium. Franzen (1977, 1979a, 1979b, and 1980 with U. Werner) arranged beads of a uniform size in various geometrical patterns, from cubical to tetragonal spheroidal. He measured the pressure drop with several Newtonian fluids, and was able to collapse the data by means of a theoretically-calculated hydraulic diameter, for Reynolds numbers up to 10^3. Franzen also tested some concentrated polymer solutions, and plotted the data in terms of the hydraulic diameter and the fluid relaxation time measured by a cone-and-plate rheometer. Because his spheres were large, 2.5 and 5.0 cm diameter, non-Newtonian effects appeared at

Reynolds numbers well above the range applicable to enhanced oil recovery. Franzen also constructed periodically-constricting channels, tested Newtonian and non-Newtonian fluids in them, and obtained results similar to the bead matrices.

The man who initiated much of the recent work on convergent-divergent flow was Payatakes. There were certainly earlier attempts, e.g. Batra et al (1970), but Payatakes' ideas seemed to catch on because inertial effects were included and because the basic cell represented a porous medium in a more realistic way. In the first paper, Payatakes et al (1973) propose not only the basic flow unit, an axisymmetric convergent-divergent channel, but also regular arrangements of such units to model a porous medium of uniform-sized grains. Later, the model is extended to allow random orientation and length of the basic unit (Payatakes & Neira, 1977). The equations are solved numerically (Payatakes et al, 1973b, Niera & Payatakes, 1977, 1978, among others), but the few concrete predictions and few comparisons with experimental data leave the reader wondering how good the model really is.

Before Payatakes, research on periodically-constricting flows generally dealt with the problem of low-Reynolds-number flow in wavy tubes. A typical example is the previously mentioned work of Batra et al (1970). Later attempts on the same sinusoidal flow problem were made by Lessen & Huang (1976) and Deiber & Schowalter (1979). In each case, the authors predict how the friction factor depends on the Reynolds number, the wavelength-to-diameter ratio and on the ratio of wave amplitude

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Kellerhalls, 1982; Szabo, 1979; and Gogarty et al, 1970). Another concern is that the polymer and surfactant interact and modify each other's performance. The surfactant can change the adsorption characteristics of the polymer (Szabo, 1979) and the interaction can cause phase separation and reduced polymer effectiveness (Szabo, 1979; Chiou & Kellerhalls, 1981). The consequences to field operations are sought in these works by laboratory tests on typical reservoir media.

11.4 New Polymers

While polyacrylamide and polysaccharide are generally the only two polymers considered for polymer flooding, other candidates are certainly available. As mentioned previously, polyethylene oxide was a candidate at one time, but the more current alternate polymers are hydroxyethyl and carboxyethyl cellulose, polyvinylpyrrolidones, cellulose sulphate esters, guar gums and scleroglucans. Szabo (1979a,b) evaluated 34 polymers (12 different types) for suitability in secondary oil recovery by comparing shear viscosity, flow resistance and retention in porous media flow. Szabo even evaluates the polymers on a cost base - one graph shows the viscosity increase per dollar of polymer. In a similar exercise, Dawson & Mentzer (1982) tested 140 polymers for viscosity retention under reservoir conditions of high temperature, pressure and salinity, and made definite recommendations for application to North Sea reservoirs. New candidates appear all the time; Goodyear, for instance, recently

developed and tested a water-soluble acrylic polymer (Klemmersen & Bauer, 1981). Because so many polymers are appearing, it will be necessary to develop laboratory techniques to quickly and reliably evaluate the suitability of new products for enchanced oil recovery.

12. SUGGESTIONS FOR FUTURE RESEARCH

A literature review generally points the way for future research, and some directions are suggested by the present review. These directions, all concerning polymer hydrodynamics, are listed below.

Some obvious directions concern the rheology of polymer solutions and the deformation of macromolecules in flowing solvents, but these have already been spelled out in Chapter 4 of Part B (Dynamics of Long Chain Polymers in Flowing Solvents). The suggestions below, then, are considered to be in addition to those in Part B.

1. A new approach could be taken to adsorption. Adsorbed chains are usually considered to cause a reduction in permeability or pore size, whereas the chains actually cause an increase in surface resistance. It is suggested that experiments be carried out to relate the increased surface resistance to the properties of the polymer, the wall and the solvent. That is, increased hydrodynamic drag caused by the adsorbed chains is expected to be a function of polymer segment density near the wall, the nature of the solvent including its ions, and the flow rate; it is not expected to be a function of polymer molecular weight according to prior research. The theoretical modelling suggested in Part A could also be applied to this situation.

2. It is apparent from Chapter 8 that fundamental research is required on the dynamics of macromolecules in pores of comparable size. The discussion in that chapter makes it clear that the processes of hydrodynamic retention, mechanical entrapment and inaccessible pore volume are not well understood. To help elucidate the underlying mechanisms, it is suggested that experiments be conducted (i) to measure the pressure or flow rate required to trap a molecule in a small channel, and (ii) to measure the pressure required to drive solvent through chains trapped in a channel or blocking an entrance. Such experiments would require polymers with narrow molecular weight distributions and micro-size filters made of a non-adsorbing material. Experiments are emphasized here because the only fundamental work on these problems so far has been theoretical.

3. Although mechanical degradation is a significant problem in polymer flooding, little is understood about the physics. Even the basic experiment of degrading PAM solutions in simple shear has not been done. Hence it is recommended that fundamental experiments on degradation be conducted first in steady shear flow and then in well-defined extensional flows.

4. Fluid particles in porous media flow undergo both shear and extension. The shear viscosity of polymer solutions has been thoroughly investigated and Part B suggested that means

be found to measure extensional viscosity, perhaps by utilizing converging channel flow at Reynolds numbers of order 10^2. Once these separate viscosity measurements are established, it would be useful to investigate combined shear and extensional deformation by studying flow in converging channels at Reynolds number less than one.

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SURVEY OF HYDRODYNAMIC EFFECTS WITH MACROMOLECULES

D. HYDRODYNAMIC EFFECTS OF POLYMERS IN FLOCCULATION

by

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1. INTRODUCTION

Method of Literature Search

The literature gathered for this review was found mainly by working backwards and forward in time from a few initial articles. Previous papers were found from the bibliographies of the first articles and then of subsequently-found articles, and more recent articles were found by using the Citation Index. This library search was augmented by a computer search; this latter method turned up little material, probably because the field is so small and the data base extends back only to 1975.

Physics of Polymer Flocculation

Polymer promotes flocculation of suspended material in water, and consequently it is widely used for waste water treatment at mining operations and in municipal waste disposal plants. The polymer helps to create aggregates of particles by forming bridges; the aggregates readily settle out because they are much larger than the individual particles and therefore no longer maintained in suspension by Brownian motion. The bridging starts when part of a polymer chain adsorbs to the surface of a particle, leaving the remaining portion free to interact with another particle. The bridging process generally does not stop at two particles, for flocs often contain scores of particles and are several hundred microns in diameter. The flocs settle

quickly and are easily removed from the bottom of a settling tank.

The term 'floc' here refers to particles held together by polymer bridges and the term 'flocculation' indicates the process. The other commonly used word is 'coagulation', and it will be used here to mean aggregation caused by the addition of simple (low molecular weight) ions to the suspension. 'Aggregation' thus refers to either or both processes. The literature is confusing because the words are often used interchangeably (a good example is the title of the major reference discussed in the next section). With our strict usage, the redundancy in the title of this section will no longer be necessary.

Summary Article

A good single reference on aggregation is the book "The Scientific Basis of Flocculation", which is the Proceedings of a NATO Advanced Study Institute (Ed: K.J. Ives, 1978). One chapter, by John Gregory, deals with polymers and is a commendable introduction to the relevant literature. The chapter covers the physics and chemistry of polymer-particle interactions, and deals with aspects such as why both charged and uncharged polymers are effective flocculants. It is a comprehensive, well-presented article, the first one to read on the subject of flocculation.

Hydrodynamics in Flocculation

The present review focusses on a non-chemical aspect of flocculation, namely, hydrodynamic effects caused by the polymer molecules. Because small amounts of polymer can generate large hydrodynamic effects in other flows – eg., reduced mobility in porous media flow (polymer flooding), or reduced friction in turbulent pipe flow – the question naturally arises regarding the importance of hydrodynamic effects in flocculation.

From the author's general knowledge of polymer hydrodynamics, it was anticipated that few references would be found on this aspect of flocculation. This indeed was the case. The hydrodynamic effects which did turn up dealt with two main topics: (i) intrinsic viscosity and its relation to polymer performance (ii) turbulence fluctuations and their role in floc formation and rupture. These topics are reviewed respectively in the next two chapters.

2. POLYMER RHEOLOGY AND FLOCCULATING EFFICIENCY

Because the polymer acts as a bridge between particles, it is not surprising to find that a polymer's effectiveness increases with molecular weight. Investigators have attempted to determine how the two quantities are related by measuring the molecular weight M_w of a polymer or, equally often, by determining its intrinsic viscosity $[\eta]$ in solution. The latter property is commonly measured because there is usually a known simple relation between M_w and $[\eta]$, and so finding the dependence of sedimentation rate, say, on $[\eta]$ is equivalent to finding its dependence on M_w. Moreover, measurments of $[\eta]$ are far easier to obtain than those of M_w.

In the first article published on this topic, J.W.M. Mackenzie (1964) measured the viscosity of polyacrylamide (PAM) solutions as a function of shear rate, pH and salt concentration, and then found the 'settling index' of flocs as a function of PAM concentration. Unfortunately there is hardly any effort to correlate the two types of measuremnts, despite the paper's title: " Relationships Between Rheological and Flocculating Properties of Polymer Flocculants". Hence the article does not seem to be of much use and probably explains why it has never been cited (according to the Citation Index).

The first solid work relating polymer performance to molecular weight was by direct measurement of M_w. Using light scattering, Anthony et al (1975) found M_w and the radius of gyration of a large variety of branched and linear PAMs. Then the optimum polymer dosage, C_{op}, of each polymer sample was found

by refiltration tests. Their findings very much conform with physical intuition: (1) C_{op} decreases as the molecular weight increases, (ii) C_{op} decreases as the radius of gyration increases, for polymers of the same molecular weight, and (iii) linear polymers are more effective than branched ones, at the same molecular weight.

Similar results were found later by Kulicke et al (1980). They too used light scattering to measure M_w, but they measured intrinsic viscosity as well. Their more complete characterization of PAM samples is not surprising, for they are part of Prof. Klein's Institute in Braunschweig where most of the basic work on $[\eta]$-M_w relations for PAM has been done. [That work is described in Sec. 2.1 of the companion review B. Dynamics of Long Chain Polymers in Flowing Solvents]. The study of Kulicke et al also differs from that of Anthony et al in that polymer performance was monitored by flocculation speed and not by optimum dosage. However, the findings of Kulicke et al are the same: flocculation increases with molecular weight, and linear PAMs are better than branched ones.

A direct correlation between sedimentation rate and $[\eta]$ was found by Wada et al in 1976, a few years before Klein's $[\eta]$-M_w relations were available. For PAM samples in the $[\eta]$ range of 4 to 23 dl/g, Wada et al found that kaolin suspensions settled at a speed which depended linearly on $[\eta]$. Such a simple result is highly attractive, but its universality has yet to be proved; tests with other polymer-particle systems are necessary to establish whether the simple relation holds in general. Chmelir

et al (1980) also measured sedimentation rate and $[\eta]$. While their results are qualitatively similar to those of Wada et al, regrettably no comparison was made.

The only theoretical work in this vein is in a paper by Walles (1968). His idea is that the absorbed polymer effectively increases the diameter of the particle, thereby altering the forces due to Brownian motion in a known way. But he does not relate the extra diametral distance to the polymer molecular weight, and so is unable to predict polymer effectiveness as a function of molecular weight. He also carried out flocculation tests which showed that settling rate varies as M_w^6, but this result should be discounted because no information is given about the measurement of M_w.

In summary, then, it appears that there may be a direct correlation between sedimentation rate (or some other measure of flocculant performance) and the rheological property intrinsic viscosity, but a more definite statement cannot be made until more experimental data are available.

3. EFFECT OF HYDRODYNAMIC SHEAR ON FLOC STRUCTURE

Turbulence plays a major role in the large stirred tanks where polymers are added to enhance sedimentation. In the initial stages, turbulence mixes macromolecules and particles, creating the close proximity necessary for bridging. But, once a floc is formed, the same turbulence can be detrimental because the agitation can break up the floc and thus slow down sedimentation. In surveying the literature, I did not come across any article which addressed these conflicting aspects of turbulence. The mechanics of break-up, however, has received some attention, and the relevant work is summarized in this chapter.

Because a floc consists of particles loosely connected by polymer strands, it is weak structurally and can readily be broken by applied forces such as tangential shear. Intuitively, one would expect that large flocs are more susceptible to rupture than small ones, and that there might be an upper bound on floc size for a given shear flow. By this reasoning one might expect that in a complex flow the maximum size of a floc is limited by the maximum shear rate it encounters, and an Australian pair has examined this mechanism in a number of articles.

In their first paper, Tomi & Bagster (1975) analyzed the hydrodynamic forces on a model floc in steady shear flow. Each model floc consisted of a number of spheres, arranged in a regular geometrical pattern and multipliably connected by linear springs. Like the Rouse model for a macromolecule, the springs

represent the linear relation between force and extension of a polymer segment. Also like the Rouse model, the shear flow is assumed to penetrate to the core of the floc and the drag on each sphere is taken to be Stokes' drag. Flocs with 6,16 and 64 particles were analyzed at various rates of shear, and in each case the largest force among the springs was found. Break-up was assumed to occur when the force exceeded an unknown but fixed rupture force. With this hypothesis, their analysis leads to the prediction that maximum floc size, d_{max}, varies as $\gamma^{-\frac{1}{2}}$, where γ is the shear rate. Unfortunately, this well-conceived theory has not been confirmed by experiment, so far as I can find. The term 'unfortunate' is used because the relation of floc size to shear rate in steady laminar shear is so important for understanding floc kinetics in more complicated flows.

Such a study would be particularly useful, for example, in interpreting work by this group and others on floc behaviour in stirred vessels. In a two-part series (1978a, 1978b), Tomi & Bagster investigated relations between floc size and turbulence length scales in tanks agitated by propellers. In the first article, they point that there is more than one length scale in a turbulent flow field. The dominant length is thought to be the macroscale, which is controlled by inertial effects, and they used scaling arguments to show that d_{max} should vary as N^{-3}, where N is the speed of the stirrer. The finest scale is the microscale, which depends on viscosity and energy dissipation, and scaling arguments showed that when the turbulence intensity is severe enough to exceed the rupture force, all flocs smaller

than the microscale should be ruptured. Because floc sizes are generally between the two length scales, the authors settled on an intermediate theory where both inertial and viscous effects are important. This led to the prediction that d_{max} varies as $N^{-1.5}$ and to a comparison with the experimental results of Reich and Vold (1959). In those expeirments, d_{max} was found to vary as $N^{-\beta}$ for a particular suspension, and, for the six suspensions studied, β varied from 0.37 to 2.5. Hence β differs considerably from the predicted value of 1.5, but is noteworthy that the average of the six β values is 1.5. Tomi & Bagster point out that the only other available theory predicts that β is 15/2. They conclude that better experimental data are called for and then, in Part II of their two-part series (1978b), they describe experiments on mineral suspensions (galena) flocculated by polyacrylamide in a stirred tank.

Their experimental study is comprehensive and well done. The extent of aggregation was detected by a turbidity meter calibrated by correlating turbidity with average floc size determined from microphotographs taken in situ. By this technique, they showed that (a) floc size initially increases with time, in a period of order minutes, and then decreases; (b) for a fixed impeller speed, the maximum floc size is independent of concentration, but the time to reach that size lengthens as the dosage drops, (c) the maximum floc size decreases with stirrer speed, (d) a floc does not reach a steady state size; that is, there is no equilibrium between aggregate rupture and

formation in a steady flow field, as there is for a coagula. Their measurements also seem to confirm their prediction that d_{max} varies as $N^{-1.5}$, i.e., floc size depends on both the macroscale and microscale in a turbulent flow field.

Two additional papers should be noted in this section. Ogendengbe (1976) investigated the performance of polyelectrolytes in sewage tanks stirred by a variable speed impeller. By dimensional arguments, the mean velocity gradient in the stirred tank was determined from impeller torque and energy input. He concluded that velocity gradients should be at least $500s^{-1}$ for satisfactory mixing and that the stirring should last about 25 minutes. This time is significantly longer than the values suggested by the work of Tomi & Bagster, but the work is noteworthy in that an estimate is given for shear rate in this turbulent flow.

The other paper is by Sylvester & Toure (1978), who were concerned with shear degradation of the polymer. Because polymer chains can be broken by excessive shear, it is possible that the high rates which promote mixing also lead to scission and therefore reduced polymer effectiveness. However, their measurements show that the time periods over which significant degradation occurs are of the order hours, and thus mechanical degradation is not likely to be a problem in water treatment plants.

4. DIRECTIONS FOR RESEARCH

This review demonstrates that only a few studies have examined the relationship between polymer hydrodynamics and flocculation. The ones that have been done, however, clearly point the way for new work. As I see it, these directions include:

1. A study of floc formation and break-up in a well-defined flow field. I find it remarkable that no one has investigated floc dynamics in the simplest and most basic of all flow fields: steady laminar shear. Such a field is not difficult to create in the laboratory and the results would aid enormously in understanding flocculation in more complex flows.

2. A study of floc formation and break-up in a well-defined turbulent flow. Turbulent motion is so complicated that fundamental studies should be conducted in flows where turbulence quantities are well known. Two such situations are axisymmetric jet flow and flow behind a grid. In these flows, there is some hope of relating flocculation to turbulence intensity, and such an investigation should logically precede studies on turbulence generated by impellers or in some other way.

3. An analysis to predict floc settling speed by treating the floc as a porous medium. The physical situation is similar

to that when macromolecules are sedimented under high gravitational forces; in that technique (used to find molecular size), the loosely-coiled macromolecule is treated hydrodynamically as a porous sphere. The same approach, with modifications, could be applied to a floc and the results should provide a theoretical framework for interpreting sedimentation data.

4. A study on the conflicting requirements of turbulence. Turbulence is needed to mix the polymer with the particles, but it also breaks up flocs. A basic study is required to analyze the turbulence intensity relevant in each process, and to find mutually advantageous regimes.

5. A study of the relation between settling speed and intrinsic viscosity for a wide variety of polymer-particle systems. Such an investigation would extend the work of Wada et al (1976) and would check the universality of the linear relation found by them for PAM-kaolin systems.

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Final Report

E. A FEASIBILITY STUDY AND DEVELOPMENT OF A FIRST MODEL OF A SETTLING VELOCIMETER

by

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Work Conducted for the Department of Energy, Mines and Resources

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1. INTRODUCTION

To effectively judge the suitability of polymers or other additives to increase the settling rates of particles in suspension, an effective means of measuring settling rates is required. The purpose of this development program is to develop an instrument capable of reliably measuring settling rates using the principle that the density of a settling suspension decreases at a rate proportional to the settling rate of the particles; and hence, can be monitored by measuring pressure differentials in a settling column.

1.1 Objectives

The principal objective of the development program is to develop a settling velocimeter (an instrument which can determine the rate, i.e. velocity, at which particles settle in a fluid) more reliably than current visual techniques used at WRL. Visual techniques involve timing of the descent of a particle/water interface and cannot detect settling within the suspension. Consequently, only the descent rate of the smallest particles can be determined. More specifically, the instrument must be able to:

a) measure settling rates of clay suspensions (Sp.Gra. 1.3) typically at 10-30% concentration by volume

b) have mixing means to create a relatively uniform concentration of particles within a settling column prior to a test

c) display the results of a test directly as a settling velocity

Objective a) was accomplished by preliminary theoretical calculations of pressure drops, suitable selection of instrumentation (pressure transducer) and actual laboratory testing.

Objective b) was attained by trial and error. Several mixing approaches were tried including a vibrating platform, stiring, tumbling and air bubbling through the column. The vibrating platform and stirrer were totally inadequate. Tumbling worked well but was impractical due to the connected pressure lines. The air bubbling through the column was judged adequate though not ideal. The air bubbling technique was finally adopted.

Objective c) was attained with difficulty. Measuring settling velocity with pressure revealed a much more complex settling behaviour than is observable visually. It was necessary to interface a microcomputer to handle the necessary signal processing and calculation. The result exceeded the original objective. The instrument is capable of measuring interface velocity, mean settling velocity, store and display data in real time and print out a permanent record.

1.2 Report Organization

The report is presented in the same chronological order as the development of the instrument. In Chapter 2, the theory is established outling the initial assumptions and verifying the theoretical feasibility of the instrument. Next, the preliminary tests are presented which were designed to reveal any technical difficulties and verify the theory. Actual test results showed the assumed theory to be too simple and demonstrated a need for a more complicated analysis. The settling model was expanded upon and a calculation technique established.

Chapter 3 details the design of the velocimeter including its mechanical, signal processing and software features. The final chapter (4) outlines a recommended operating procedure covering mixing, calibration and actual running of the experiment.

2. BACKGROUND THEORY AND VERIFYING TESTS

This chapter provides an outline of the initial feasibility analysis, verifying tests and subsequent refinement of a theoretical model carried out prior to the actual design and construction of the prototype velocimeter. It covers the work carried out by S & J Engineering Inc. from October 1982 to the end of March 1983 and forms the foundation upon which the design details are based.

2.1 Basic Theory

A schematic of the settling velocimeter is shown in Figures 1 and 2. A column filled with a suspension in water to the level Z = 0 has a particle water interface at Z_a, two pressure ports at Z_b and Z_c and pressure lines filled with water connected to a differential pressure transducer.

In Figure 1, the interface is above the pressure port at Z_b, while in Figure 2 it is between the ports. The third possible case where the interface is below Z_c ($P_1 = P_2$ and $\Delta P = 0$) is of no interest since the velocimeter can only make settling measurements when the interface is between or above the pressure ports.

2.1.1 Particle Interface Above Pressure Ports

In Figure 1, the transducer measures a differential pressure head $\Delta P = P_1 - P_2$ where

$$P_1 = P_0 + \gamma_w Z_a + \gamma_s (Z_b - Z_a) + \gamma_w h_2$$

and $$P_2 = P_0 + \gamma_w Z_a + \gamma_s (Z_b - Z_a) + h_3\gamma_s - h_4\gamma_w$$

where P_0 = atmospheric pressure

γ_w = Sp. gravity of water = 1

γ_s = Sp. gravity of the suspension

substituting $\gamma_w = 1$ gives

$$\Delta P = P_1 - P_2$$
$$= (h_2 + h_4) - h_3\gamma_s$$
$$= h_3(1 - \gamma_s)$$

which shows that the differential pressure is proportional to the distance between the pressure ports and $(1 - \gamma_s)$. As the particles settle, γ_s decreases to γ_w (i.e., 1) and then ΔP drops to 0 as if the column just contained water. γ_s, the average specific gravity of the suspension between the pressure ports can be further broken down as

$$\gamma_s = \alpha\gamma_p + (1 - \alpha)\gamma_w = \alpha\gamma_p + 1 - \alpha$$

where α is the volumetric concentration of particles and γ_p is the specific gravity of the particles hence

$$\Delta P = \alpha h_3(1 - \gamma_p)$$

For any given suspension, γ_p is constant as is h_3, hence ΔP varies only as a function of the average particle concentration α. If the particles drop at a uniform rate, then while the particle interface is above the upper pressure port, there will be an equal amount of particles entering and leaving the region between the ports and the measured pressure differential will be a constant since α is constant. Even when the particles do not fall uniformly, particles entering the top pressure port region will balance most of the particles leaving below the lower port, causing at most small changes in pressure. This would suggest that while the particle interface is above the upper pressure port and pressure differential cannot directly measure a settling velocity. This implies that settling velocities can only be measured when the particle interface lies between the pressure ports. As tests carried out of settling clay suspensions show, these assumptions are too simple. Before presenting actual test data and a subsequently refined theoretical model the basic theory for the case when the particle interface is between the pressure ports will be presented.

2.1.2 Particle Interface Between Pressure Ports

In Figure 2, the pressure ΔP (cm of water) measured by the differential pressure transducer is:

$$\Delta P = P_1 - P_2 \text{ where}$$

$$P_1 = P_0 + \gamma_w h_1 + \gamma_w h_2$$

$$P_2 = P_0 + \gamma_w h_1 + \gamma_w (h_3 - h_6) + \gamma_s h_6 - \gamma_w h_4$$

where P_0 = atmospheric pressure

γ_w = Sp. gravity of water = 1

γ_s = Sp. gravity of the suspension

thus

$$\Delta P = P_1 - P_2$$

$$= \gamma_w h_3 - \gamma_w (h_3 - h_6) - \gamma_s h_6$$

$$= h_3 - h_3 + h_6 - \gamma_s h_6 = h_6 (1 - \gamma_s)$$

and since

$$\gamma_s = \alpha \gamma_p + (1 - \alpha)\gamma_w = \alpha \gamma_p + 1 - \alpha$$

where α = Volumetric concentration of particles

and γ_p = Specific gravity of particles

then

$$\Delta P = \alpha h_6 (1 - \gamma_p)$$

Once again, ΔP only depends on the particle specific gravity, the particle volumetric concentration and the proportion of the column height between the ports filled with the suspension. For a uniform concentration of particles below the interface, both α and γ_p are constant consequently $\Delta P \alpha h_6$ and therefore the rate of change of ΔP is directly proportional to the rate of change of h_6 which is the particle settling velocity.

Figure 3 shows the expected behaviour of ΔP versus time showing both the behaviour while the interface is above the upper port (ΔP constant) and while the interface is falling between the ports (ΔP decreasing to 0).

2.2 Experimental Verification

Before the actual design and construction of the velocimeter took place, tests were conducted to verify that actual behaviour of settling suspensions were as initially expected. The first exploratory tests conducted during November and December of 1982 in which the optimum mixing technique and general configuration and layout was determined are not presented though the results are summarized below in 2.2.1. The final tests which directly relate to the velocimeter as finally designed are presented in 2.2.3.

2.2.1 Test Apparatus

A test apparatus was set up as shown schematically in Figure 4. It consisted of a long column almost 1 metre in length and 2 centimeters internal diameter, an enlarged overflow and filling trap on top, an air inlet at the bottom and pressure taps at spaced intervals along the column.

The air inlet was provided to blow air into the column to mix the particles and create a pseudo uniform suspension. From earlier tests, this was found to be the most effective mixing means since vibration and shaking were totally inadequate and tumbling of the column was awkward with the pressure lines connected.

The choice of a 2 cm ID column was arbitrary. A larger diameter column would have required an unnecessarily large volume

of suspension while a smaller column would have been much more difficult to clear.

The upper enlarged diameter funnel was provided as a convenient spout for filling purposes and an overflow trap sufficiently large to prevent the suspension from overflowing during the air mixing.

The pressure port to port distance was set at 20 cm so as to provide a sufficiently large pressure differential for the transducer available at clay volumetric concentrations as low as 5%.

The transducer was a variable inductance type of very high sensitivity capable of resolving pressure changes as low as 0.1 mm of water. (Specification Sheet in Appendix C.)

2.2.2 Experimental Procedure

The experimental procedure adopted for all tests was as follows. First, a polymer solution was prepared to the correct concentration by dilution from a fully dissolved master solution of a neutral 100 ppm polyacrylamide (Provided by WRL). This solution was then mixed in a beaker with clay so that the resultant concentration (by weight) of the clay suspension was 10%. (Earlier tests with varying clay concentrations showing similar results

are not shown here since they were carried out using a more primitive and hence redudant apparatus.) After mixing, the suspension was poured into the column with the air

supply turned on low to maintain a uniform concentration of particles.

With the suspension slowly mixing, the transducer was balanced (for 0 shift) and the pressure lines checked for air. When everything looked in order, the air mixing valve was closed, the pressure lines opened and the experiment started. In addition to monitoring the differential pressure with time, the location of the particle interface level was recorded.

2.2.3 Experimental Results

Figures A1 through A5 (Appendix A) show the results of five settling tests of a 10% by weight suspension of clay in concentrations of 0, 2, 4, 8 and 16 ppm neutral polyacrylamide solutions. All the data show similar behaviour; a pressure differential starting at 0.75 cm decreasing slowly to 0.55 cm. differential and then more rapidly to 0.0 cm while the particle interface from visual observation drops at a very uniform rate. The initially slower drop of ΔP corresponds to the period in which the interface is observed to be above the upper port while the more rapid descent occurs while the interface drops between the ports. As expected, the pressure difference approaches 0.0 as the interface nears and then passes the lower port. The initial pressure differential is constant reflecting a uniform concentration at the beginning of each test proportional to the particle concentration. Settling velocity during the period of more rapid descent is simply 20 cm. (port to port distance)

divided by the descent time. Results from numerous other tests at other concentrations using other clay samples and other polymers show striking similarity.

2.2.4 Discussion of Results

The analysis of 2.1 predicted a uniform pressure differential followed by a steady drop. This prediction is not much different from that observed but for one detail. In all tests, the pressure differential falls even while the interface lies above the upper port indicating that there is measurable settling of larger particles within the suspension of smaller particles. This is also confirmed by observations that larger coarser grains settle on the bottom of the column followed by successively smaller particles. It becomes clear that in order to obtain a complete understanding of the settling behaviour, the settling velocity and pressure differentials must be knwon from the time $t = 0$. This can be done by knowing the pressure differential from the surface of the suspension to the lower port either from direct measurement or by extrapolation.

2.2.5 Data Extrapolation

Refering to Figure 1, the ratio of the total height above the lower port to the port to port distance is given by:

$$\frac{h_1 + h_3}{h_3} = 1 + \frac{h_1}{h_3}$$

At time t = 0, the differential pressure ΔP measured between the ports, when multiplied by this factor would give the differential pressure extrapolated to the surface. For each t > 0, up to the time that the interface drops below the upper port (t_b), the extrapolated pressure differential is:

$$\Delta P^* = \Delta P + \frac{h_1}{h_3}\left(\frac{t_b - t_1}{t_b}\right)\Delta P \qquad \text{for } 0 \leq t \leq t_b$$

The factor $(t_b - t)/t_b$ is a linearly decreasing factor accounting for the dropping of the interface (which is observed to drop uniformly). The time t_b if not directly observed, can be closely approximated as:

$$t_b = \frac{h_1}{h_1 + h_3}\, t_c$$

where t_c is the total time for the pressure to drop to 0 (interface passes lower port).

In Figures A1 to A5, the extrapolation as outlined above has been carried out. As is apparent, the extrapolated data when combined with the remaining pressue data form a continuous curve and give a complete history of both settling velocity and density (ΔP).

2.2.6 Settling Velocity

Three measures of settling velocity are obtainable from the pressure diffential versus time behaviour of a settling column. They are:

a) Instantaneous settling velocity V_i

b) Mean settling rate V_{mean}

c) Interface velocity v_I

In principal, the instantaneous settling velocity is immediately obtainable from the slope of the ΔP versus t curve since from 2.1.2

$$V_i \alpha \frac{d\Delta P}{dt}$$

In practice, however, the scatter in ΔP is too large to make V_i particularly meaningful. For the purposes of this report, the issue is settled by ignoring this velocity altogether and working only with a mean velocity and an interface velocity.

To obtain the mean settling velocity for a test, the following measure is used.

$$V_{mean} = \frac{2x \text{ Mean height from which particles have dropped}}{\text{total descent time}} = \frac{zh_d}{t_d}$$

where the mean height from which the particles have dropped is taken as the mean pressure differential measured above the lower port (averaged against time) relative to the initial pressure differential measured multiplied by the column height, i.e.:

$$h_d = \frac{\Delta P_{mean}}{\Delta P_0}(h_1 + h_3)$$

from which

$$V_{mean} = \frac{2\Delta P_{mean}}{\Delta P_0 \; t_d}(h_1 + h_3)$$

If this measure seems somewhat arbitrary, it is because V_{mean} is actually a mean mass flux since the mean pressure differential is a measure of the average density of particles in the column.

The interface velocity is quite simply

$$V_I = \frac{h_1 + h_3}{t_d}$$

which is identical to V_{mean} if the particles settle uniformly, i.e.:

when $\frac{\Delta P_{mean}}{\Delta P_0} = \frac{1}{2}$ (uniform settling)

then $V_{mean} = V_I$

ΔP_{mean} is obtained by integration of ΔP versus t_p and t_d from the time required for the pressure differential to drop to 0.

3. VELOCIMETER DESIGN

The velocimeter consists of six basic parts, a settling column, a pressure measuring transducer interconnecting electronics and a microcomputer to monitor and analyse the test. A schematic of the device is given in Appendix A, Figure 4.

3.1 Mechanical Design

3.1.1 Settling Column

The settling column is a 2 cm I.D. tube almost 1 metre in height with an airline connected to the bottom (for air mixing of the suspension) three pressure taps spaced 20 cm apart along its length and a 6 cm I.D. overflow and filling trap on its upper end. This column is identical to that described earlier in 2.2.1.

3.1.2 Transducer

The transducer is a very high resolution variable inductance type of differential transducer made by Celesco, Model P7D. It was chosen for its combination of high sensitivity, ruggedness and stability over time. A specification sheet for this transducer is given in the appendix.

3.1.3 Interconnecting Piping

Between the settling column, the transducer and the manometer there are a series of interconnecting tubes and valves. They allow connection and disconnection of the settling column to the transducer, air traps, zeroing valves for checking proper transducer operation and connecting means between the transducer and manometer.

3.1.4 Manometer

The manometer is a water air type allowing for up to 50 cm differential head of water. The output of the transducer in volts should be one fifth of the differential head of water in cm.

3.2 Signal Processing

Connected to the pressure transducer is a carrier demodulator (CD10) which converts the signal from the transducer into a linear voltage proportional to the differential pressure. There are two control knobs on the CD10, a "zero" potentiometer and a "gain" potentiometer. The "zero" potentiometer is used to zero the output voltage on the transducer when the differential pressure is known to be zero. This will occur whenever valves A or B on the interconnecting piping are opened. This compensates for any hysteresis or electronic drift effects which could given

an erroneous reading. All tests involve pretest "zeroing" and after test 0 checks. The "span" knob of the CD10 controls the amplification of the signal from the transducer so that the output voltage can be set to any convenient multiple of the pressure (within limits). Before shipping, the transducer was set to yield a voltage proportional to 1/5 of the pressure in cm of water. (Although, strictly speaking, the velocimeter only requires that the voltage from the transducer is proportional to the actual pressure differential, we recommend that periodic checks be made to insure that this value does not drift appreciably).

From the CD10, the signal passes to an ADC (Analog to Digital Converter) board located in slot 2 of the UNITRON microcomputer. The input is prefiltered since the signal from the CD10 is quite noisy with the signal to noise ratio in the range of our measurements reaching as much as 20%. This filter simply integrates the CD10 signal over time then averages and amplifies the value. Three integration intervals are provided 256, 512 and 1,024 ms and are controlled using switches 1b, 2b and 3b (Fig. 5.1.2). Because the computer program operates on a 256 msec cycle, the 256 msec integration interval is used (all switches 1b, 2b and 3b on). The signal amplification is also variable and can be set to either 1, 2 or 4 using switches 1a, 2a and 3a. The program assumes no signal amplification (gain = 1) with all of switches 1a, 2a and 3a on.

Once the signal has been suitably filtered and averaged, it is stored in a sample and hold (S/H) circuit which stores the

filtered value in analog form until it is updated (every 256 msec in our case). As soon as the value is updated, the A/D converter is triggered, the signal is digitized and sent to the computer memory by the machine language routine NEW CODE. Routine TRANSLATE retrieves this data for processing.

Greater technical detail on the circuitry is given in Appendix C.

3.2.1 Microcomputer

The UNITRON microcomputer used to process and evaluate the velocimeter data is an Apple "clone", i.e.: it is both hardware and software compatible with any Apple 1le computer and uses the same peripheral devices and operating systems. A D.O.S. operating system is used with the UNITRON and all software is written in either machine language or Apple Basic.

3.2.2 Peripherals

The UNITRON requires at least one disk drive connected to it to operate the software. A dot matrix printer (EPSON FX80 or equivalent) may also be added to obtain hard copy of data and graphs. The software is already incorporated to print as necessary.

NOTE: A printer interface card in slot 6 is also required when operating an FX80 or other printer.

3.3 Software

The software package is self-explanatory and highly interactive. At every stage of the experiment, the operator is given detailed instructions, after which the program waits for acknowledgement before proceeding to the next step. The most common operational problems will be detected by the computer, which will then direct the user to take appropriate action, or refer to the documentation. Flowcharts showing the structure of the programs are given in Appendix D.

The five programs on the Master Disk are:

HELLO - Identifies the disk and allows user to run an experiment or access the UTILITY program. HELLO is run automatically at power-up.

A/D START - Collects experiment parameters and prepares system to run an experiment. A/D START may be run by the user.

MAIN - Monitors the experiment; collects data; processes and adjusts data; and creates data file. MAIN will not run correctly unless it is called by A/D START.

UTILITY - Displays contents of files formed by MAIN; copies and prints data files as requested. UTILITY may be run by the user.

NEW CODE - Machine language program used by MAIN and A/D START to read the pressure transducer. NEW CODE is not accessible to the user.

With the Master Disk in the disk drive at power-up, the HELLO program is run immediately. This allows the user to either start an experiment or access data files with the UTILITY program, by pressing a single key. The user may also write his own programs, after exiting HELLO.

3.3.1 A/D START Program

The A/D START program has two functions: it first gathers information from the operator about the test, and then instructs the operator to zero the system (see flowchart, Appendix D).

Prompts appear on the screen whenever the operator is required to make an entry. After the port and fluid levels have been input, and the zeroing valve opened, the operator is instructed to adjust the zero dial of the carrier demodulator until a zero is read by the ADC board. The operator then closes the zero valve and opens the equilization valve so that A/D START can check for air in the pressure lines.

Once the zeroing and air check is completed, test parameters are stored in a temporary file (called ZZYZZX) for transfer to the MAIN program, which is then loaded into the micro and run.

The MAIN program performs 3 tasks concurrently as it monitors the experiment (see flowchart, Appendix D): as each pressure reading is received, it is plotted on the screen, a counter is incremented to keep track of the time elapsed, and the pressure reading is stored in an array for analysis at the end of the run.

The program will detect at what point the pressure differential has reached zero, or, if the voltage at the ADC does not go to zero, at what point the suspension above the lower port reached its steady-state condition. The elapsed time at this point becomes T, the total experiment time, and is used as the basis for much of the data analysis which follows.

After the experiment has terminated, the operator is instructed to open the zero valve, so the program can check to see if the zero point has drifted. If it has, the data points in memory are adjusted by the amount

$$-\frac{t}{T} Z$$

where t is the experiment time corresponding to the point being adjusted

and Z is the change in the ADC reading with value A open, over the time t = 0 to t = T.

Finally, the data is extrapolated, processed, stored in a data file and replotted on the screen. Control is then passed back to the HELLO program.

3.3.2 Utility

UTILITY is an entirely interactive program whose function is only to display and copy the data files created by the MAIN program. All commands available to the user at any given time are displayed on the screen and can each be implemented by pressing one key.

The main instruction set of UTILITY, and the effects of each command are as follows:

P - plots data on screen as it appeared after processing in original run

E - prints the above plot as it appears on screen; P must be called before for any given run

N - allows operator to examine a new data file without restarting the program

C - allows operator to copy data files under the original file name (for back-up) or a new file name (for re-naming files)

L - lists all specific parameters and results of the run, and allows user to access the data points themselves, or to print any of this information

X - stops execution of the UTILITY program.

See also UTILITY Flowchart (Appendix D).

3.3.3 New Code and Translate

The machine language routine "NEW CODE" is the MAIN and A/D START programs' link to the experiment. The A/D interface board converts the transducer voltage to digital signals, which are the only type the computer itself can use. The machine language routine is initialized at the start of MAIN and A/D START, and called whenever a data point is required. When called, NEW CODE waits until the converter is ready to supply a reading, and then stores this reading in memory. The subroutine TRANSLATE, in MAIN and A/D START (lines 10-150) retrieves this data by 4 PEEKS and then, using a table, converts it to an integer, equal to 1000 times the transducer voltage. This integer is stored in variable V, for use by the rest of the program.

If the user wishes to write his own program to use NEW CODE and translate, he should refer to Appendix C.

4. USERS GUIDE

The following section is intended to provide a rough guide as to how to setup and use the settling velocimeter.

4.1 Setup/Operation

(a) Mount Velocimeter board vertically on a wall firmly secured with C-clamps or screws.

(b) Fold out the carrier demodulator CD10 (on platform) and secure all connecting electrical cables (4 per plug between transducer and demodulator, 3 per plug between demodulator and UNITRON).

(c) Connect a Voltimeter to the output of the demodulator and turn on demodulator (voltmeter should be on 2 volt range).

(d) Turn "zero" dial on the demodulator. If the voltmeter reading changes, good; if not, check cable connections for electrical faults.

(e) Disturb the pressure transducer (squeezing plastic tubing near the transducer). If the pressure (voltage reading) changes, good; if not, check cable connections.

(f) Fill all of the interconnecting piping with clean water and remove all air (particularly in valve bores).

(g) Turn on the Unitron and follow the instructions on the screen. The computer will lead you through the pretest and test sequences.

4.2 Mixing Suspensions

All suspensions should be thoroughly premixed (with polymer) prior to testing. After pouring into the settling column a low pressure air supply should be connected to the air mixing inlet (5 psi max) and the air allowed to bubble gently through the

mixture. This will maintain a uniform suspension. Too much air will cause spillage and spray from the top of the column and degrade any polymer in solution. The air mixing should be continued until all the pretest sequences have been completed (as indicated by the program). The valves from the settling column should remain closed during air mixing to prevent air from entering the pressure lines. It is not recommended to rely on the air mixing to create a uniform suspension after settling has already occurred. The air should be shut off and the valves from the settling column opened to begin a velocimeter test.

4.3 Transducer Calibration

Selector valves located just above the transducer allow the transducer to be connected either to the settling column or the manometer. To calibrate the transducer turn the selector valves to the manometer and follow this sequence (connect CD10 and Multimeter as before).

(a) Open valve A.

(b) Turn "zero" dial on the demodulator until output voltage reads 0.

(c) Close valve A and pour water into one of the two manometer tubes.

(d) Read the differential pressure in cm of water.

(e) Turn the "span" dial on the demodulator until the desired fraction of voltage (1/5 of the differential head in cm for example) is attained.

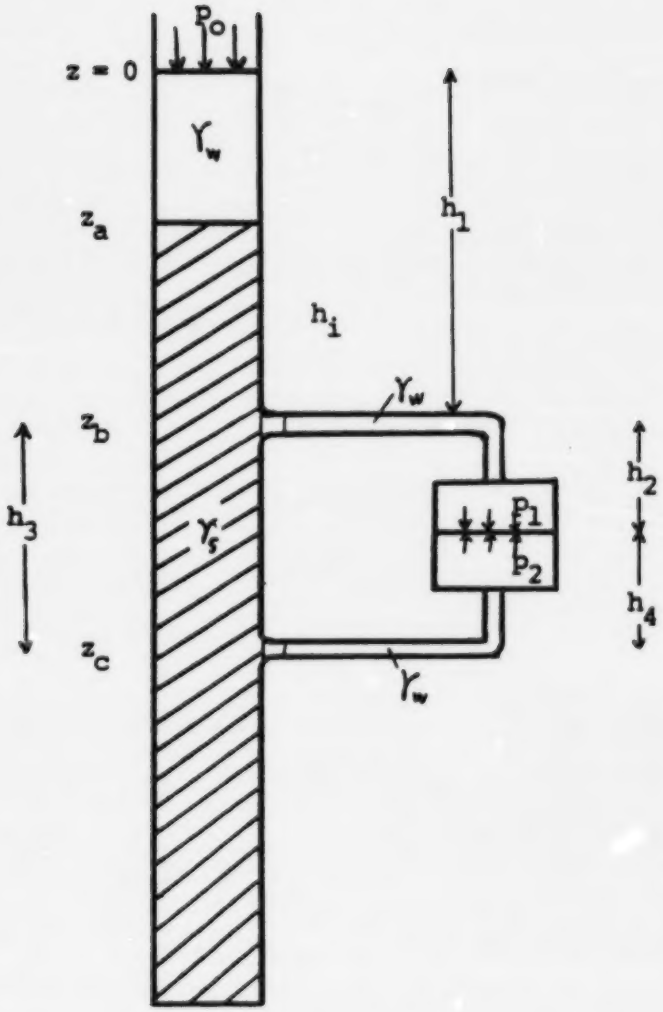
(f) Open valve A (column should move and stop when level with each other).

(g) The output voltage should again read 0. If not, repeat the entire sequence.

NOTE: It is not necessary to calibrate the transducer for operation of the velocimeter. Settling velocities and data processing only require proportional changes in pressure to work properly.

APPENDIX A

FIGURES



γ_s = specific wt. of suspension

γ_w = specific wt. of water = 1

γ_p = specific wt. of particles

$$\gamma_s = (1 - \alpha)\gamma_w + \alpha\gamma_p$$

$$= 1 - \alpha + \alpha\gamma_p$$

α = concentration (volumetric)

FIGURE 1

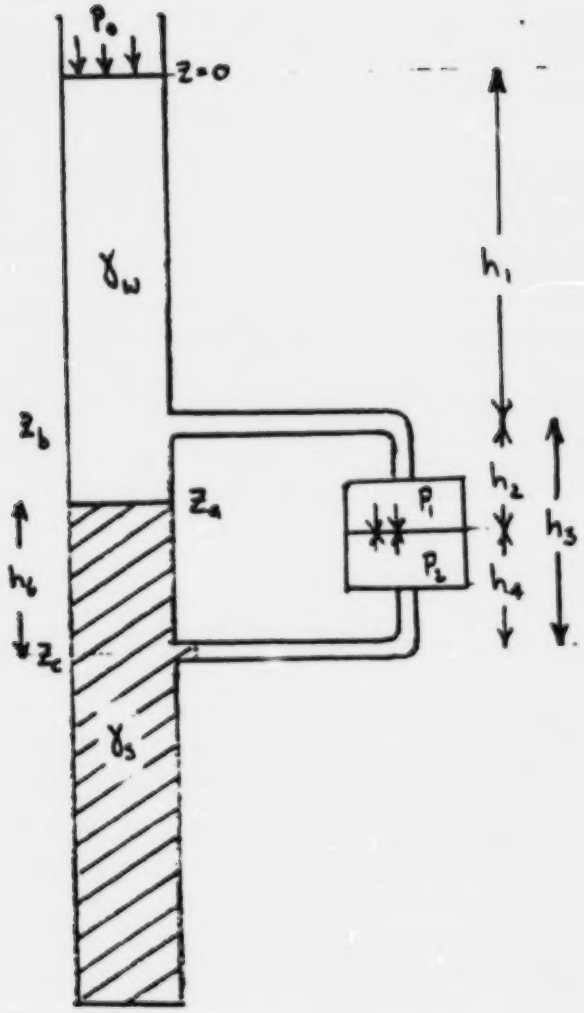


FIGURE 2

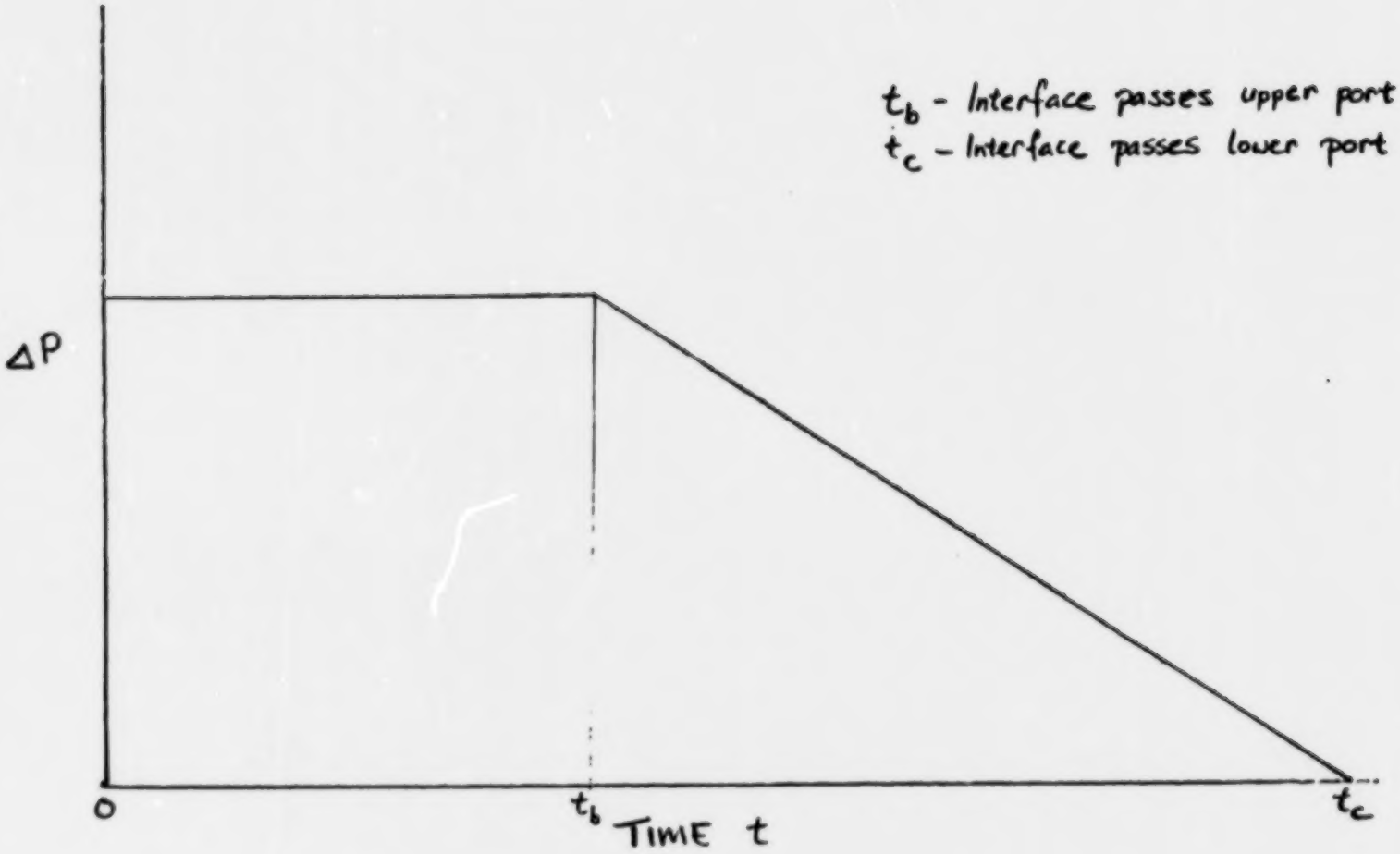

t_b - Interface passes upper port
t_c - Interface passes lower port
ΔP
0
t_b
TIME t
t_c

FIGURE 3

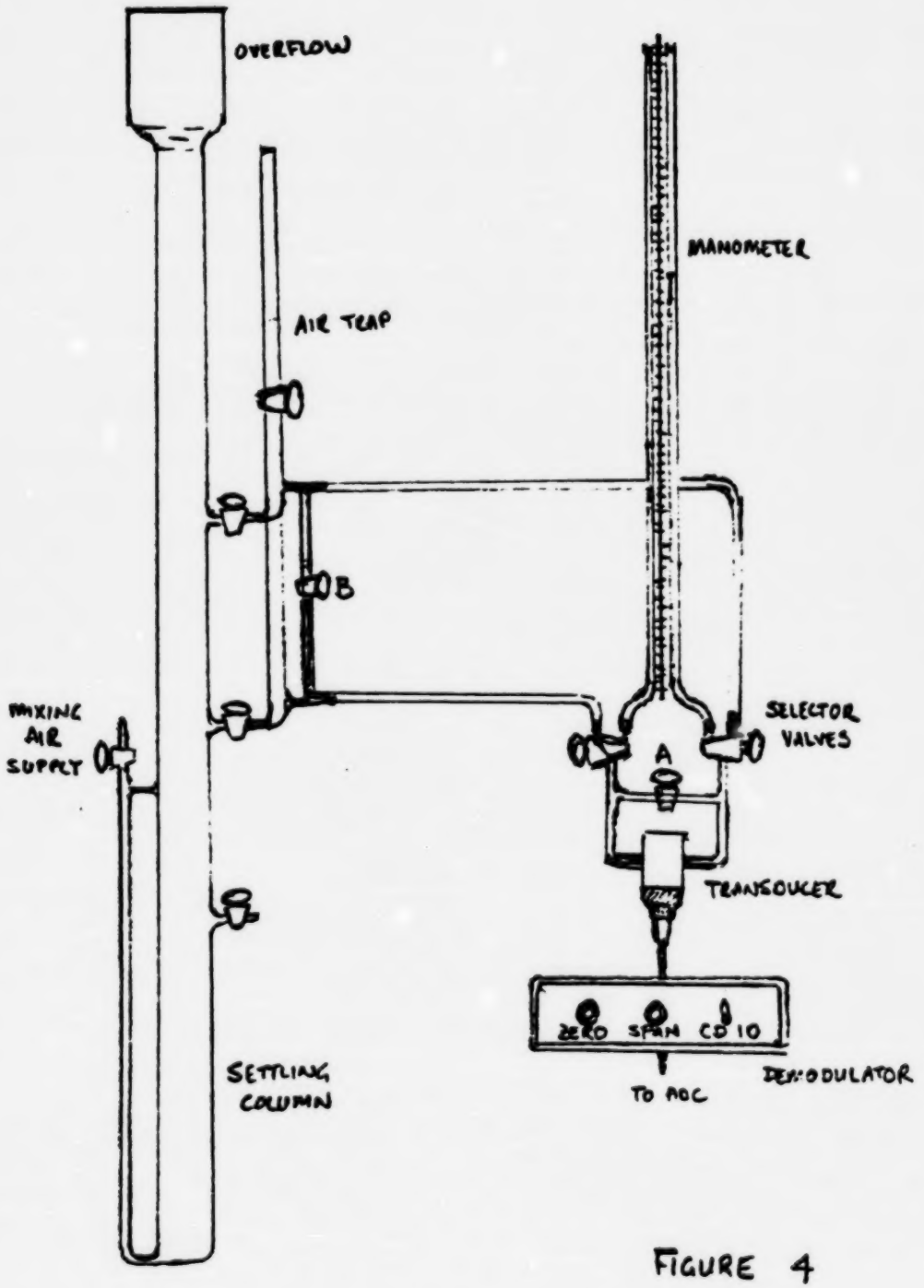
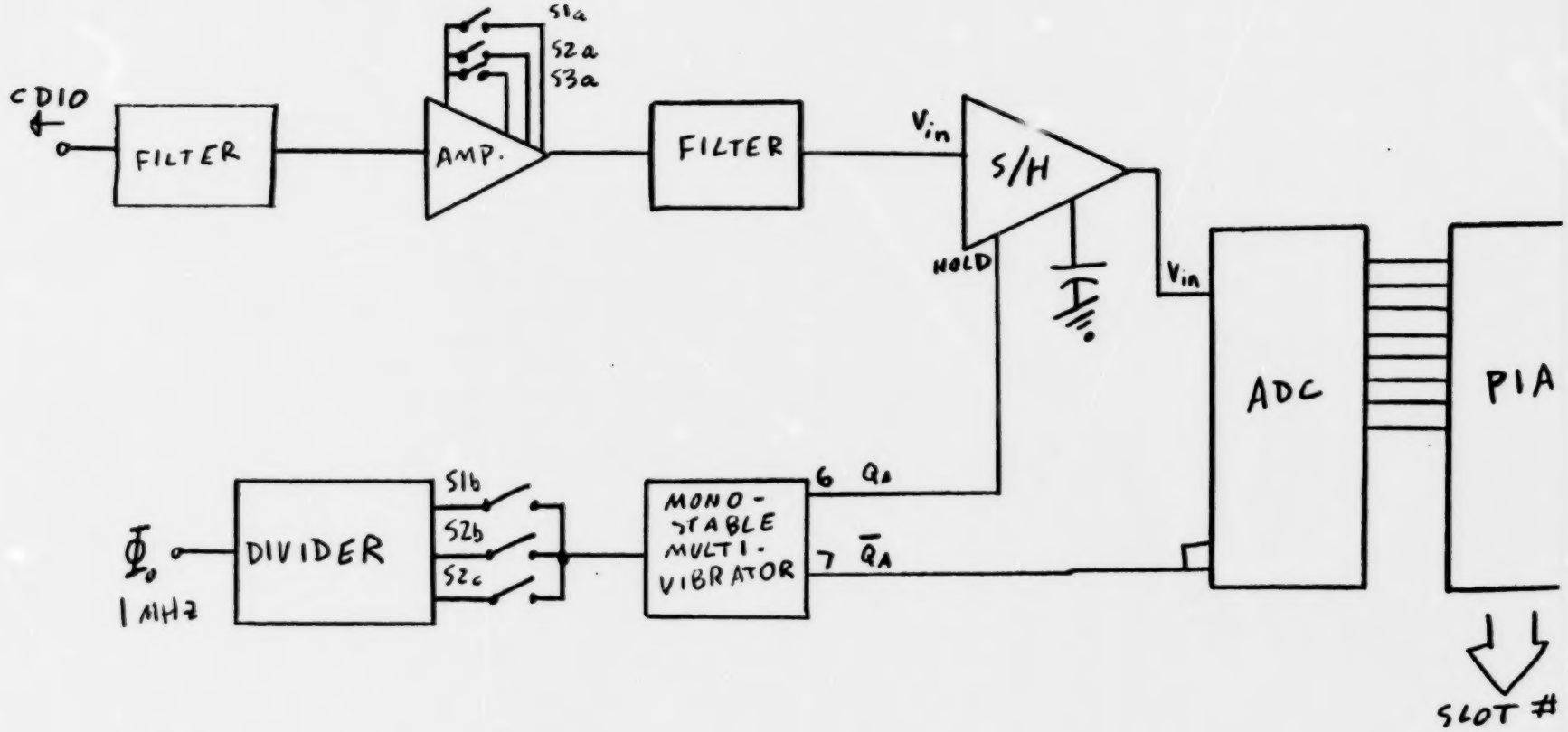
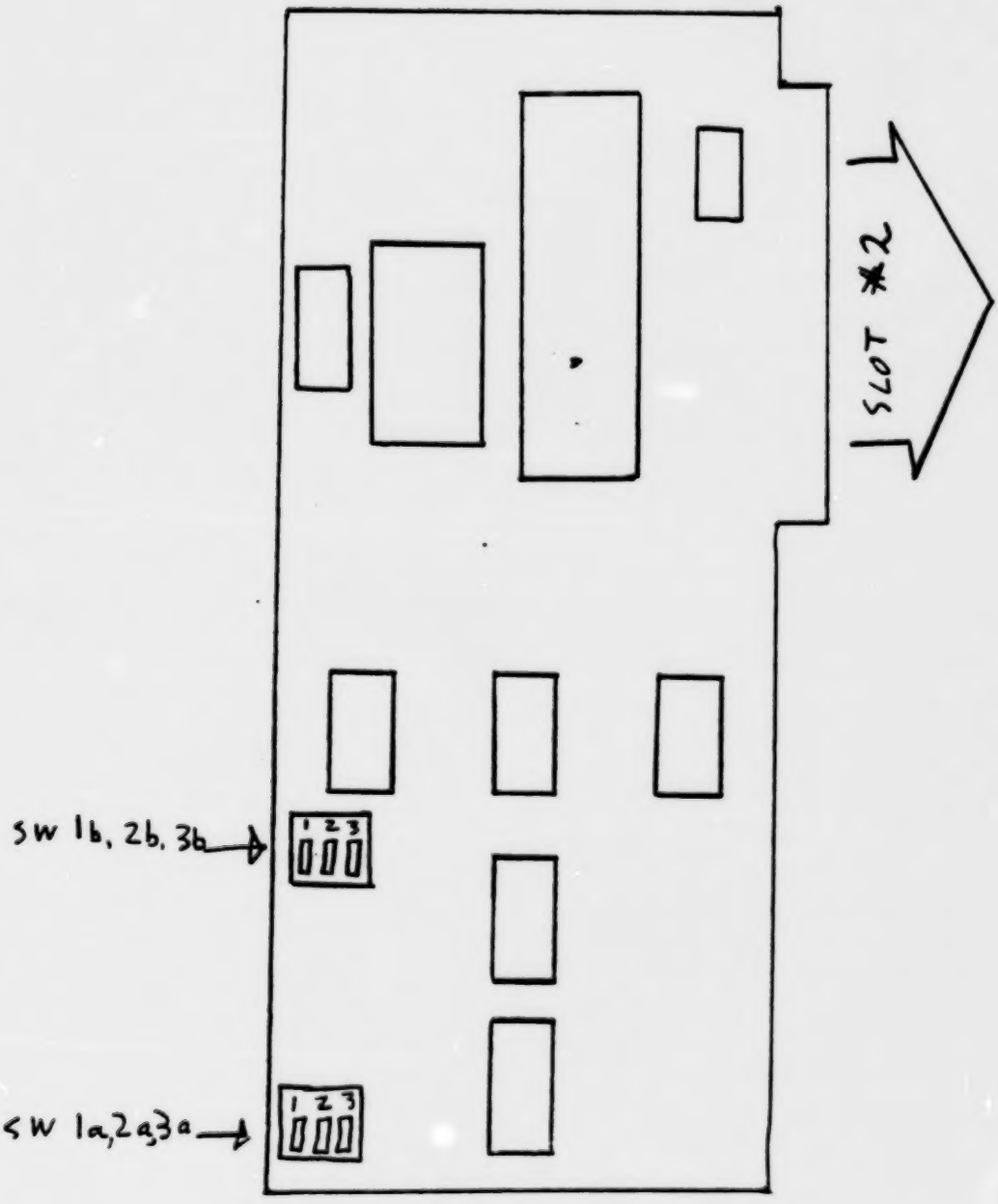

OVERFLOW
AIR TRAP
MANOMETER
B
MIXING AIR SUPPLY
SELECTOR VALVES
A
TRANSDUCER
ZERO
SPAN
CD 10
DEMODULATOR
TO ADC
SETTLING COLUMN

FIGURE 4



ADC BOARD BLOCK DIAGRAM

FIGURE 5.1



ADC BOARD LAYOUT

FIGURE 5.2

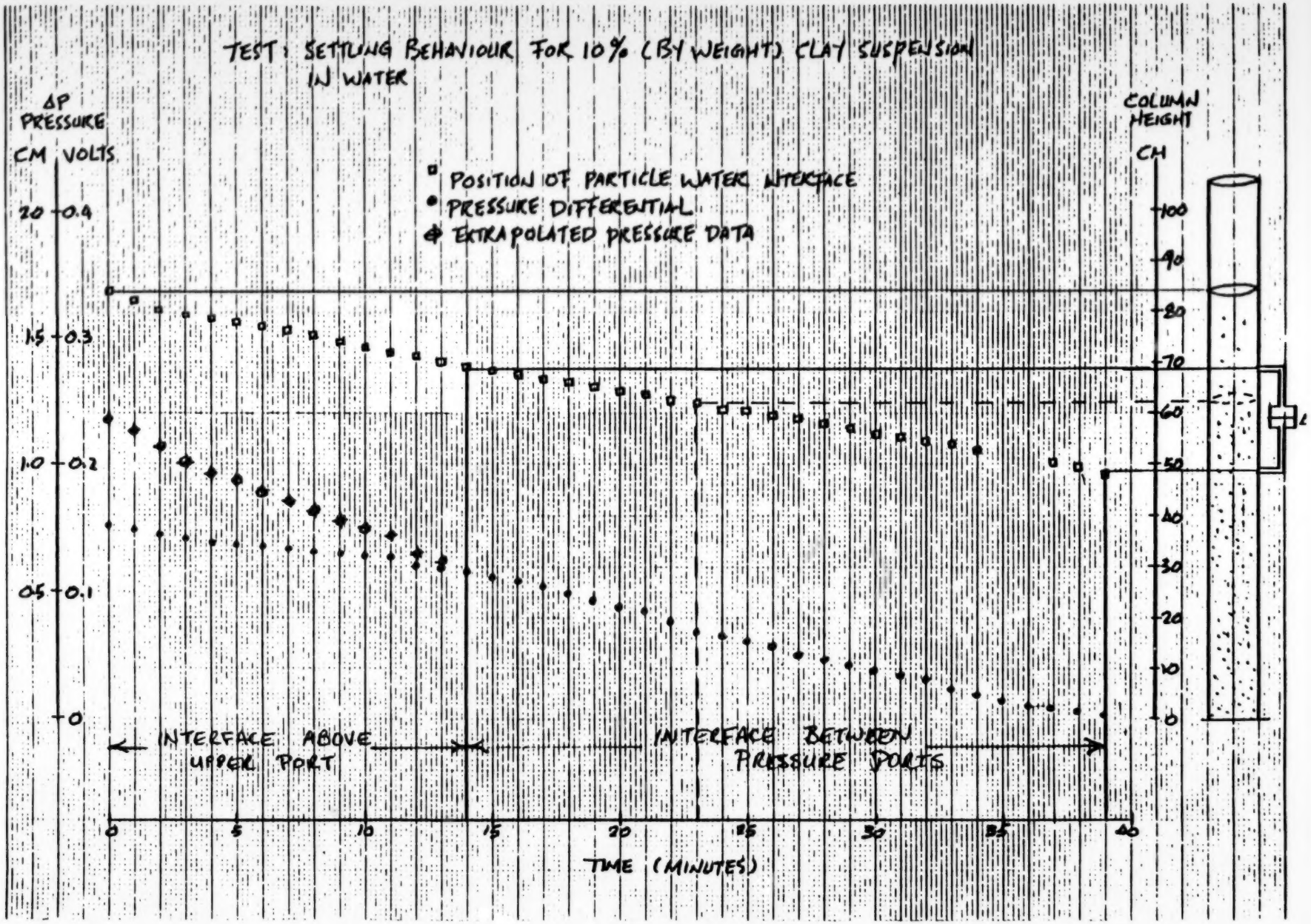

TEST: SETTLING BEHAVIOUR FOR 10% (BY WEIGHT) CLAY SUSPENSION IN WATER
ΔP PRESSURE
CM VOLTS
20 0.4
1.5 0.3
1.0 0.2
0.5 0.1
0
POSITION OF PARTICLE WATER INTERFACE
PRESSURE DIFFERENTIAL
EXTRAPOLATED PRESSURE DATA
COLUMN HEIGHT
CM
100
90
80
70
60
50
40
30
20
10
0
INTERFACE ABOVE UPPER PORT
INTERFACE BETWEEN PRESSURE PORTS
0
5
10
15
20
25
30
35
40
TIME (MINUTES)

FIGURE A1

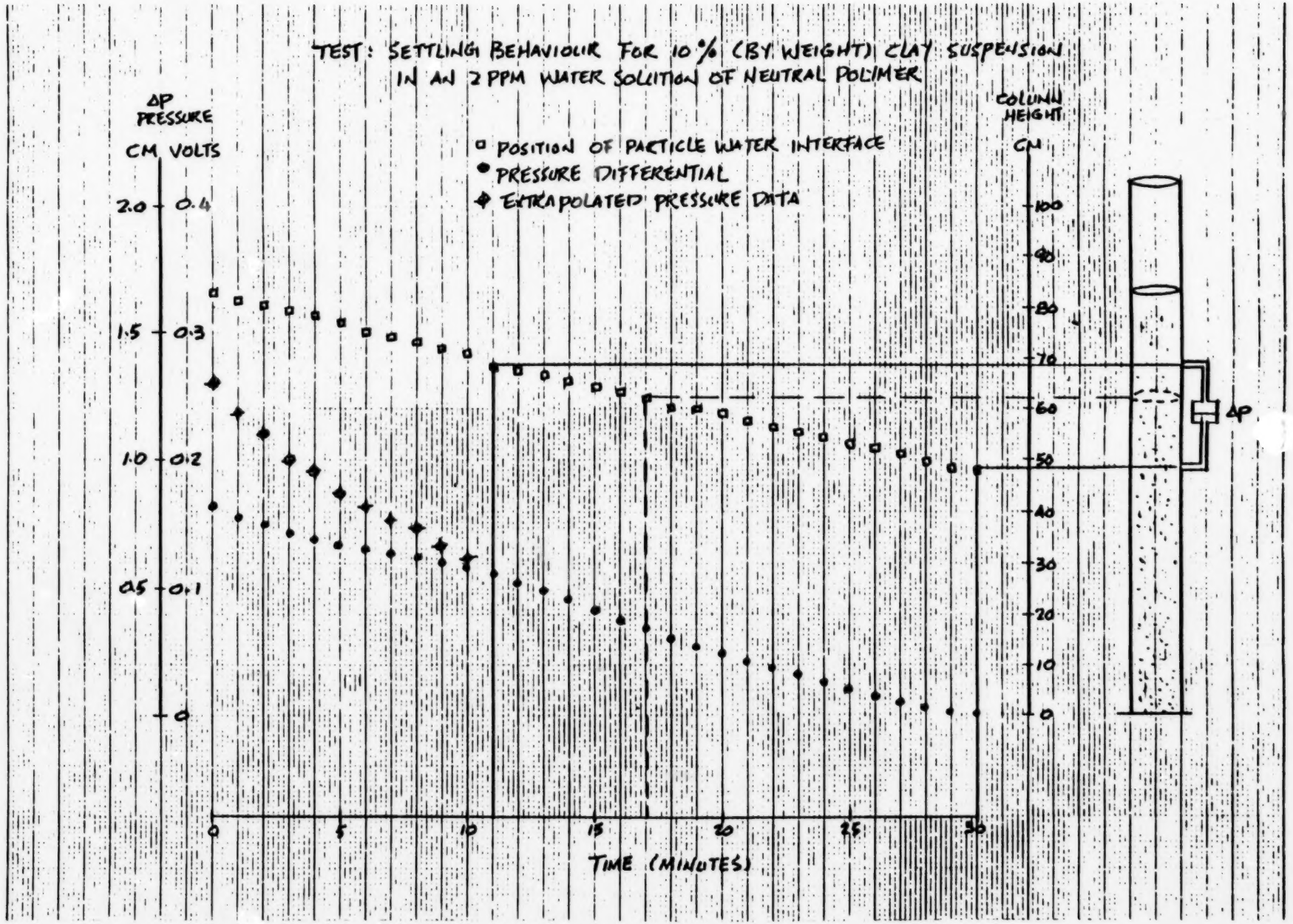

TEST: SETTLING BEHAVIOUR FOR 10% (BY WEIGHT) CLAY SUSPENSION IN AN 2 PPM WATER SOLUTION OF NEUTRAL POLYMER
ΔP PRESSURE CM VOLTS
COLUMN HEIGHT CM
□ POSITION OF PARTICLE WATER INTERFACE
● PRESSURE DIFFERENTIAL
◆ EXTRAPOLATED PRESSURE DATA
2.0
1.5
1.0
0.5
0
0.4
0.3
0.2
0.1
100
90
80
70
60
50
40
30
20
10
0
ΔP
0
5
10
15
20
25
30
TIME (MINUTES)

FIGURE A2

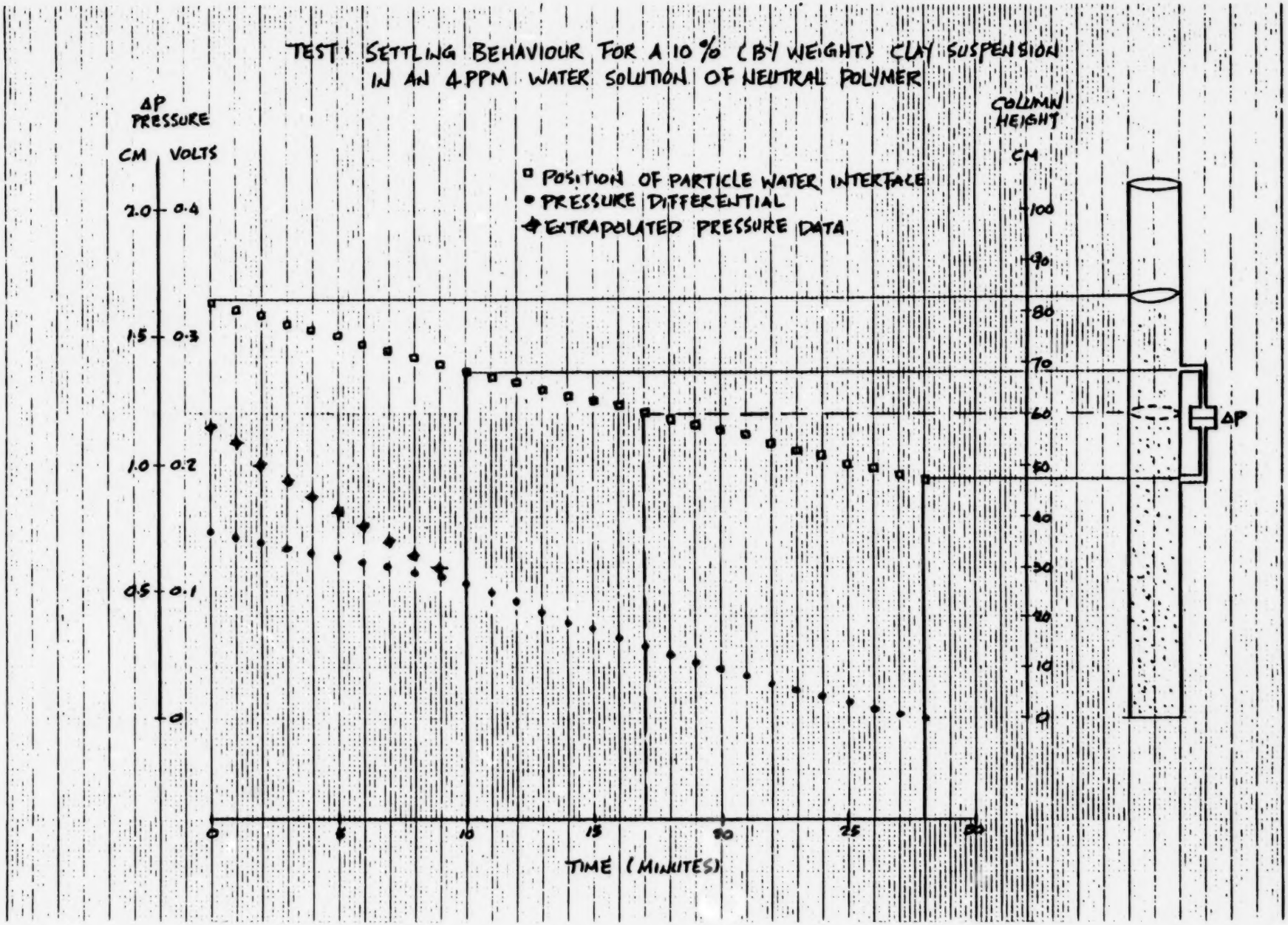

TEST: SETTLING BEHAVIOUR FOR A 10% (BY WEIGHT) CLAY SUSPENSION IN AN 4PPM WATER SOLUTION OF NEUTRAL POLYMER
ΔP PRESSURE
CM
VOLTS
2.0
0.4
1.5
0.3
1.0
0.2
0.5
0.1
0
POSITION OF PARTICLE WATER INTERFACE
PRESSURE DIFFERENTIAL
EXTRAPOLATED PRESSURE DATA
COLUMN HEIGHT
CM
100
90
80
70
60
50
40
30
20
10
0
ΔP
0
5
10
15
20
25
30
TIME (MINUTES)

FIGURE A3

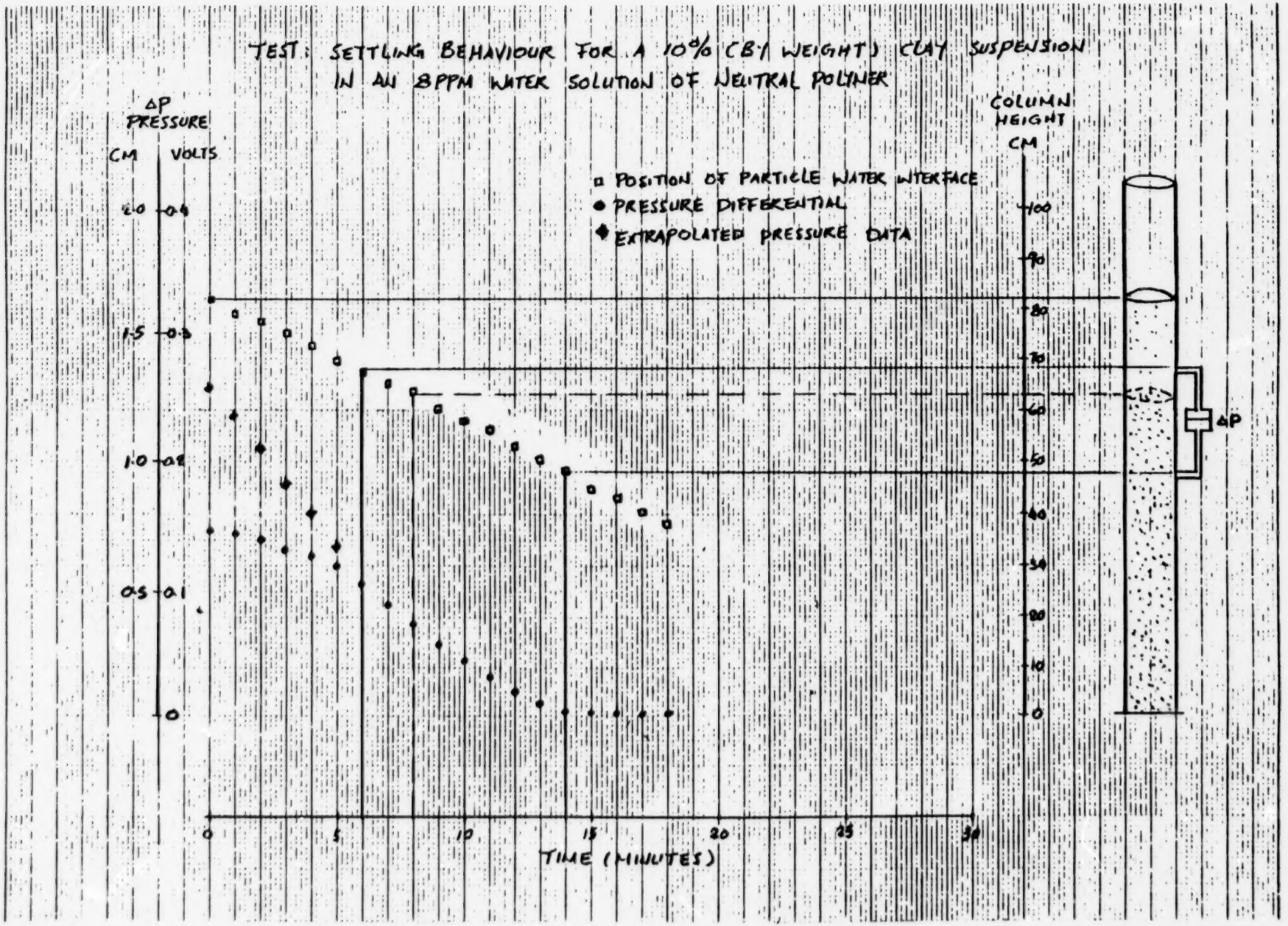

TEST: SETTLING BEHAVIOUR FOR A 10% (BY WEIGHT) CLAY SUSPENSION
IN AN 8PPM WATER SOLUTION OF NEUTRAL POLYMER
ΔP
PRESSURE
CM
VOLTS
2.0
1.5
1.0
0.5
0.4
0.3
0.2
0.1
0
□ POSITION OF PARTICLE WATER INTERFACE
● PRESSURE DIFFERENTIAL
◆ EXTRAPOLATED PRESSURE DATA
COLUMN
HEIGHT
CM
100
90
80
70
60
50
40
30
20
10
0
ΔP
0
5
10
15
20
25
30
TIME (MINUTES)

FIGURE A4

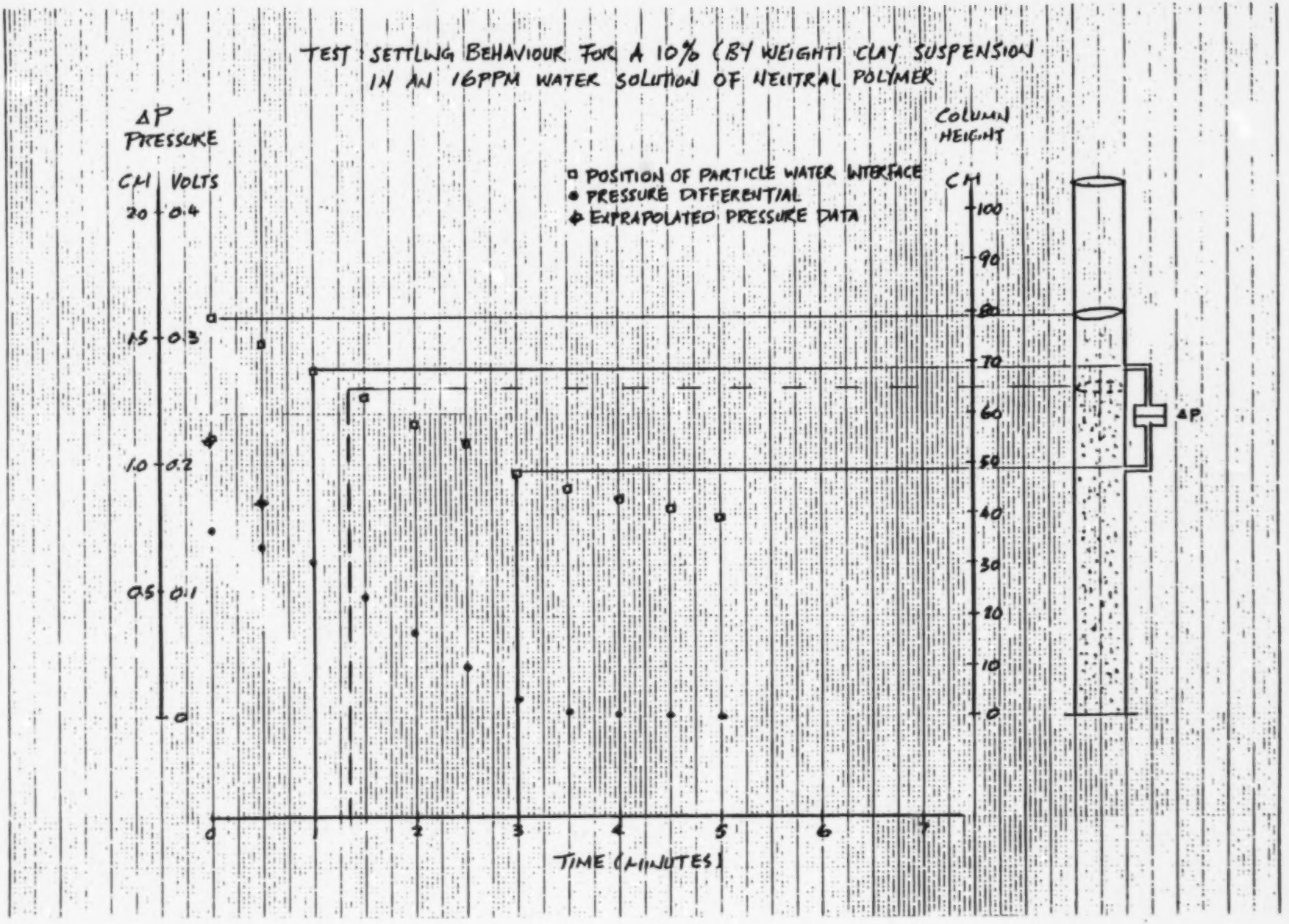
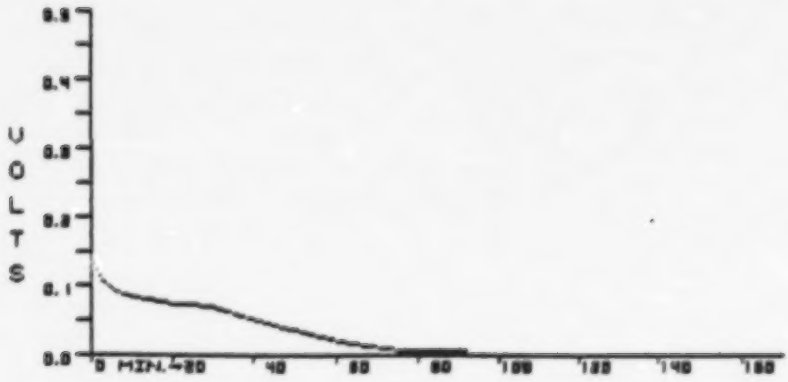

TEST : SETTLING BEHAVIOUR FOR A 10% (BY WEIGHT) CLAY SUSPENSION IN AN 16PPM WATER SOLUTION OF NEUTRAL POLYMER
ΔP PRESSURE
CM
VOLTS
20
0.4
1.5
0.3
1.0
0.2
0.5
0.1
0
POSITION OF PARTICLE WATER INTERFACE
PRESSURE DIFFERENTIAL
EXTRAPOLATED PRESSURE DATA
COLUMN HEIGHT
CM
100
90
80
70
60
50
40
30
20
10
0
ΔP
0
1
2
3
4
5
6
7
TIME (MINUTES)

FIGURE A5

A P P E N D I X B

Sample Data from Unitron



unprocessed data→

EXPERIMENT PARAMETERS:
TEST: JUNE14/4

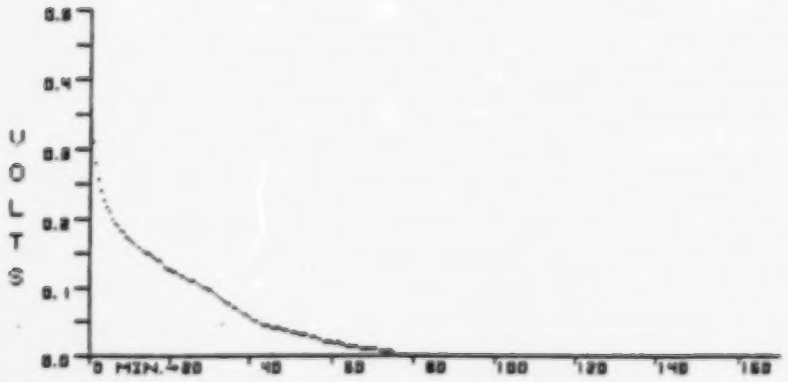
FLUID LEVEL	(LA)=	41CM.
UPPER PORT LEVEL	(LB)=	15.68CM.
LOWER PORT LEVEL	(LC)=	-2.9CM.
SAMPLING INTERVAL	(TB)=	41.104SEC.
INITIAL V. (ADJ.)	(PO)=	.309V.
MEAN SETTLING TIME	(SP)=	1244.2SEC.
TIME ELAPSED	(ET)=	4521SEC.
INITIAL MASS FACTOR	(MF)=	384.4V.SEC.

MEAN SETTLING VEL. (SV)= .0176CM/SEC

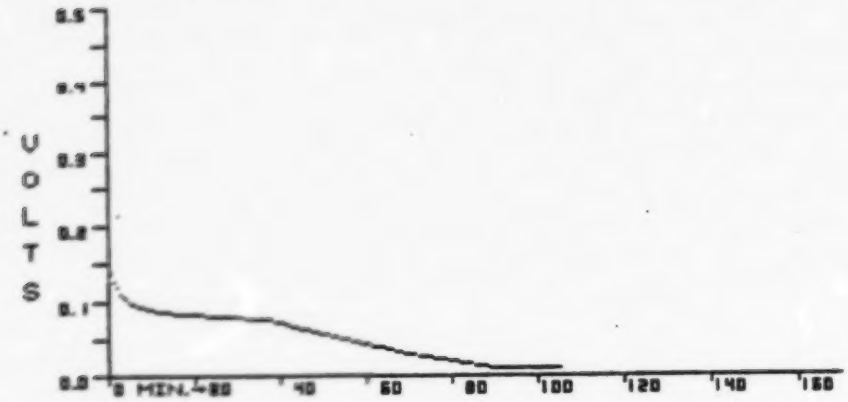
MEAN INTERFACE VEL. (IV)= 9.7E-03CM/SEC

5 VOLTS <==> 1 CM. HEAD

TEST: JUNE14/4



TEST: JUNE15/2



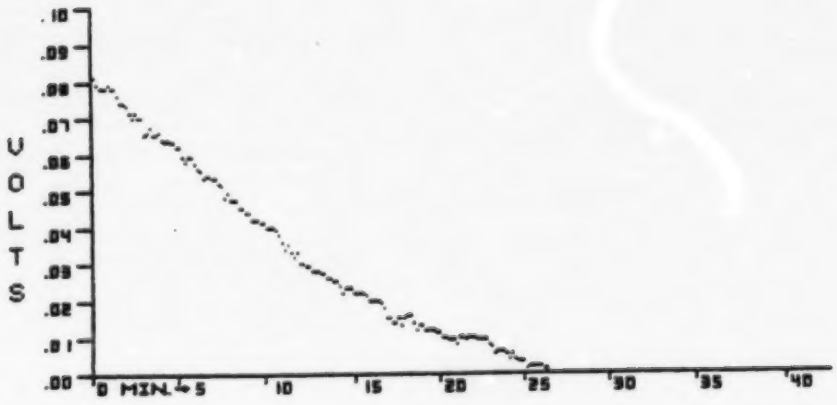
unprocessed data-*

EXPERIMENT PARAMETERS:
TEST: JUNE15/2

FLUID LEVEL	(LA)=	45CM.
UPPER PORT LEVEL	(LB)=	16.8CM.
LOWER PORT LEVEL	(LC)=	-2.9CM.
SAMPLING INTERVAL	(TB)=	41.104SEC.
INITIAL V. (ADJ.)	(PO)=	.328V.
MEAN SETTLING TIME	(SP)=	1518.2SEC.
TIME ELAPSED	(ET)=	5344SEC.
INITIAL MASS FACTOR	(MF)=	497.9V.SEC.
MEAN SETTLING VEL.	(SV)=	.0157CM/SEC
MEAN INTERFACE VEL.	(IV)=	8.9E-03CM/SEC

5 VOLTS <==> 1 CM. HEAD

TEST: JUNE1/2



EXPERIMENT PARAMETERS:
TEST: JUNE1/2

FLUID LEVEL	(LA)=	28CM.
UPPER PORT LEVEL	(LB)=	15.68CM.
LOWER PORT LEVEL	(LC)=	-2.9CM.
SAMPLING INTERVAL	(TB)=	10.276SEC.
INITIAL V. (ADJ.)	(PO)=	.081V.
MEAN SETTLING TIME	(SP)=	652.9SEC.
TIME ELAPSED	(ET)=	1839SEC.
INITIAL MASS FACTOR	(MF)=	52.7V.SEC.
MEAN SETTLING VEL.	(SV)=	.0236CM/SEC
MEAN INTERFACE VEL.	(IV)=	.0168CM/SEC

5 VOLTS <==> 1 CM. HEAD

PROCESSED DATA (READ ACROSS)
TEST: JUNE1/3

TIME (SEC)	V.OUT (VOLTS)	TIME (SEC)	V.OUT (VOLTS)	TIME (SEC)	V.OUT (VOLTS)	TIME (SEC)	V.OUT (VOLTS)
0	.115	10.2	.114	20.5	.111	30.8	.111
41.1	.108	51.3	.108	61.6	.105	71.9	.105
82.2	.102	92.4	.1	102.7	.101	113	.099
123.3	.098	133.5	.096	143.8	.096	154.1	.095
164.4	.093	174.6	.092	184.9	.092	195.2	.091
205.5	.089	215.7	.087	226	.088	236.3	.086
246.6	.085	256.8	.085	267.1	.084	277.4	.084
287.7	.081	298	.081	308.2	.08	318.5	.078
328.8	.076	339.1	.076	349.3	.075	359.6	.075
369.9	.074	380.2	.072	390.4	.072	400.7	.071
411	.071	421.3	.07	431.5	.068	441.8	.068
452.1	.066	462.4	.067	472.6	.067	482.9	.065
493.2	.064	503.5	.064	513.7	.062	524	.061
534.3	.061	544.6	.061	554.9	.059	565.1	.057
575.4	.057	585.7	.056	596	.056	606.2	.055
616.5	.056	626.8	.057	637.1	.055	647.3	.055
657.6	.053	667.9	.053	678.2	.052	688.4	.049
698.7	.049	709	.05	719.3	.048	729.5	.048
739.8	.047	750.1	.047	760.4	.047	770.7	.046
780.9	.047	791.2	.045	801.5	.042	811.8	.041
822	.041	832.3	.04	842.6	.04	852.9	.04
863.1	.038	873.4	.038	883.7	.037	894	.036
904.2	.036	914.5	.035	924.8	.034	935.1	.035
945.3	.034	955.6	.034	965.9	.034	976.2	.034
986.4	.033	996.7	.033	1007	.033	1017.3	.032
1027.5	.032	1037.8	.031	1048.1	.03	1058.4	.031
1068.7	.029	1078.9	.029	1089.2	.029	1099.5	.029
1109.8	.028	1120	.027	1130.3	.027	1140.6	.027
1150.9	.026	1161.1	.026	1171.4	.026	1181.7	.025
1192	.025	1202.2	.025	1212.5	.024	1222.8	.024
1233.1	.023	1243.3	.023	1253.6	.024	1263.9	.022
1274.2	.022	1284.5	.022	1294.7	.02	1305	.02
1315.3	.019	1325.6	.019	1335.8	.019	1346.1	.018
1356.4	.017	1366.7	.016	1376.9	.016	1387.2	.016
1397.5	.015	1407.8	.014	1418	.014	1428.3	.014
1438.6	.014	1448.9	.012	1459.1	.012	1469.4	.012
1479.7	.012	1490	.012	1500.2	.011	1510.5	.012
1520.8	.011	1531.1	.011	1541.4	.01	1551.6	.01
1561.9	.01	1572.2	.01	1582.5	.01	1592.7	9E-03
1603	9E-03	1613.3	8E-03	1623.6	8E-03	1633.8	8E-03
1644.1	8E-03	1654.4	8E-03	1664.7	7E-03	1674.9	6E-03
1685.2	6E-03	1695.5	6E-03	1705.8	6E-03	1716	6E-03
1726.3	6E-03	1736.6	6E-03	1746.9	6E-03	1757.1	5E-03
1767.4	5E-03	1777.7	4E-03	1788	4E-03	1798.3	3E-03
1808.5	4E-03	1818.8	3E-03	1829.1	3E-03	1839.4	3E-03
1849.6	3E-03	1859.9	3E-03	1870.2	2E-03	1880.5	1E-03
1890.7	0	1901	0	1911.3	0	1921.6	0

A P P E N D I X C

Components - Detailed Data

APPENDIX C

Components - Detailed Data

The ADC interface card consists of two parts, the sample-and-hold (SAH) and analog-to-digital converter (A/D). The functional and operational details of A/D are given as follows:

The A/D is constructed by using a Motorola monolithic analog to digital converter MC14433 and a Motorola peripheral interface adapter (PIA) MC6821. The PIA provides interfacing between computer and the A/D converter. It also detects the timing strobe from SAH. The input voltage range of A/D is 0-1.999 V and is accurate to within 1 lsd. Its conversion rate is approximately 1 per 65 ms. With SAH running at a minimum rate of 262 ms, the software has about 200 ms for data manipulation and storage in the worse case.

Hardware Description

Schematic 1 shows the circuit diagram of SAH.

Schematic 2 shows the circuit diagram of A/D. The computer recognizes A/D as four memory locations: $CON0 through $CON3 (N stands for the slot number which the interface card is plugged into), and these are the locations of registers of the PIA. The PIA communicates with MC14433 via its port B and the handshake lines CB1 and CB2. CB2 sends a display-update strobe to the MC14433 for the latest result and CB1 receives a strobe from

MC14433 for data ready. Since MC14433 outputs its data in BCD form (through 00, 01, 02 AND 03), it is necessary to determine which digit is available, and this is done through PB7-DS1, PB6-DS2, PB5-DS3 and PB4-DS4 pairs. The program reads port B and checks each of its bits to determine which digit is available (PB7 through PB0 are bits in a byte of port B and PB7 is the most significant digit). Timing signal from the SAH is routed to CA1 and PA7, where CA1 detects a positive going pulse and PA7 detects a holding digital 1.

The rest of the circuit is a voltage reference which supplies a stable reference voltage of 1.999 V to MC14433 pin 2. Pins 4, 5, 6, 7, 8, 10 and 11 are for the conversion frequency. Pin 3 is for analog input and pin 1 is the analog ground. Power supplies are pin 12 for -5 V, pin 24 for 5 V and pin 13 is for the ground. In this circuit, analog and digital ground are tied together. The single inverter 74LS04 is for address decoding of PIA.

Functions of the four registers of PIA:

(1) $CON0 and $CON2 – these two memory locations serve dual purposes, (i) to declare data direction, and (ii) to act as data input/output port. During initialization of PIA, they are data direction registers. One can designate any bit in any of the ports as an input or output bit. In this present design, they are all inputs. After the initialization, they become data I/O ports and are referred as PA and PB respectively.

2) $CON1 and $CON3 – these two memory locations provide accesses to the two control registers of the PIA. By writing proper data to it, one can:

   (a) change the role of $CON0 or $CON2 to either one of their functions,

   (b) send TTL signal to other circuits via CA2 or CB2.

After reading the registers, one detects incoming strobe. it 7 of control register is on when a strobe is detected. A hotocopy is attached with this report that gives detail escroption of the functions of control registers.

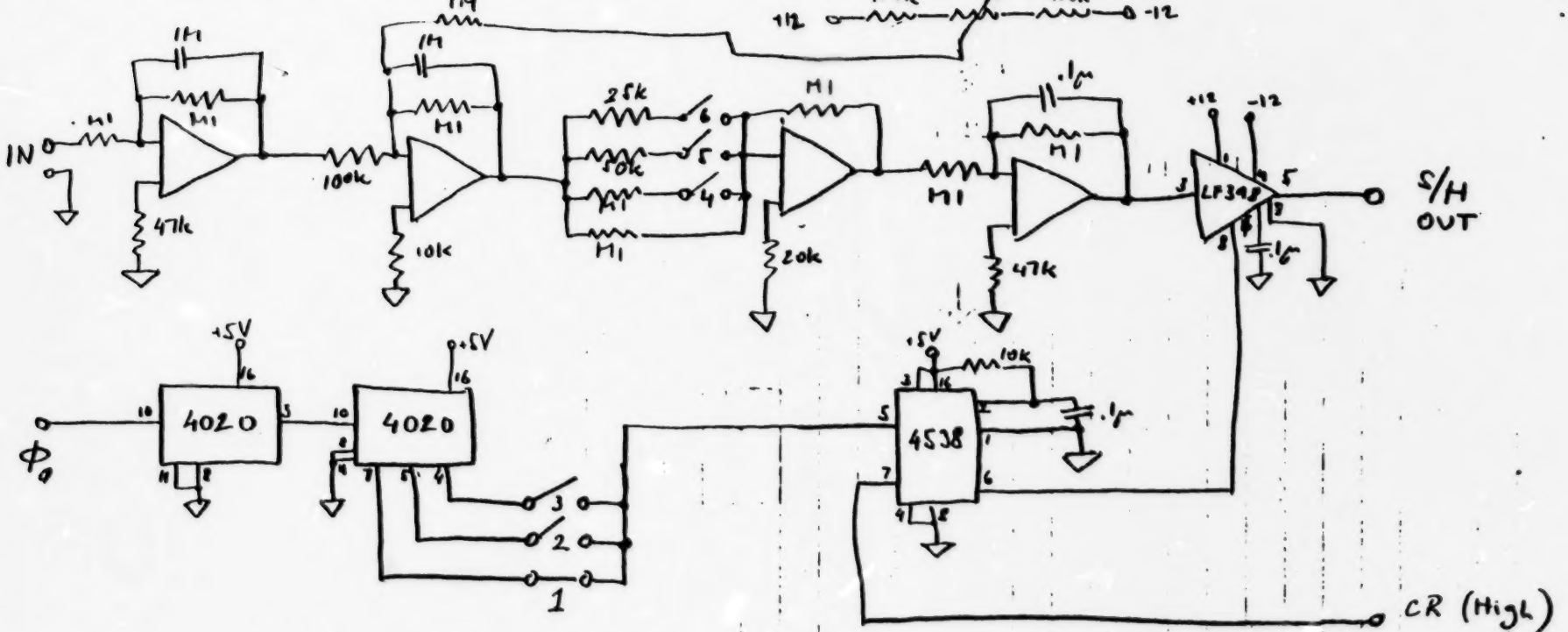
Program Description

Two programs are provided to demonstrate the interface card. he first one is a machine language routine written to perform ata conversion, and it stores result in computer memory for further processing. The other program uses ADC and the screen as digital voltmeter. Listings 1 and 2 are the programs and they are self-explanatory.

```
LISA 2.5

0816 F0 F9       22          BEQ START          :IF NOT RECEIVED. GO BACK
0818 AD A0 C0    23          LDA DATA1          :SEEMS TO BE IN
081B 6A          24          ROR                :CHECK PA7 TO BE SURE
081C 90 F3       25          BCC START          :IF FALSE TRIGGERING. GO BAC
TO CHECK AGAIN
081E A9 3F       26          LDA #$3F           :THIS IS FOR REAL. TELL A/D T
 UPDATE DATA
0820 8D A2 C0    27          STA CR2
0823 A9 37       28          LDA #$37           :READY STROBE FOR NEXT ONE
0825 8D A2 C0    29          STA CR2
0828 AD A2 C0    30  EOC     LDA CR2            :PURGE THE OLD DATA HELD IN A
E
082B 29 80       31          AND #$80
082D F0 F9       32          BEQ EOC            :JOB DONE?
082F AD A2 C0    33          LDA DATA2          :YES. OK TO CLEAR REG FOR NEX
 STROBE
0832 A9 3F       34          LDA #$3F           :OK THIS TIME IS FOR REAL
0834 8D A2 C0    35          STA CR2            ;TELL THE CONVERTER
0837 A9 37       36          LDA #$37           :CLEAR STROBE FOR NEXT ONE
0839 8D A2 C0    37          STA CR2
083C AD A2 C0    38  EOC1    LDA CR2            :IS NEW DATA READY YET
083F 29 80       39          AND #$80
0841 F0 F9       40          BEQ EOC1           :WAIT UNTIL IT IS
0843 AD A2 C0    41  FIDI    LDA DATA2          :OK DATA IS IN: CHECK FOR FIR
T DIGIT
0846 0A          42          ASL
0847 90 FA       43          BCC FIDI           :IF NOT THERE.WAIT FOR IT
0849 18          44          CLC                : IT IS THERE!
084A 6A          45          ROR
084B 85 06       46          STA $06            :STORE THE VALUE THEN
084D AD A2 C0    47  SEDI    LDA DATA2          :IS SECOND ONE READY YET
0850 0A          48          ASL
0851 0A          49          ASL
0852 90 F9       50          BCC SEDI           :IF NOT. WAIT FOR IT
0854 18          51          CLC
0855 6A          52          ROR
0856 6A          53          ROR                :IT IS IN. SAVE IT
```

```
085C 0A          56              ASL
085D 0A          57              ASL
085E 0A          58              ASL
085F 90 F8       59              BCC THDI          :DON'T MIND TO WAIT FOR IT
0861 18          60              CLC               :OK IT IS IN
0862 6A          61              ROR
0863 6A          62              ROR
0864 6A          63              ROR
0865 85 08       64              STA $08           :SAVE IT!
0867 AD A2 C0    65  FODI        LDA DATA2         :OK THIS IS THE LAST ONE
086A 0A          66              ASL
086B 0A          67              ASL
086C 0A          68              ASL
086D 0A          69              ASL
086E 90 F7       70              BCC FODI          :IT IS IN YET
0870 18          71              CLC               :GOOD. IT IS THERE
0871 6A          72              ROR
0872 6A          73              ROR
0873 6A          74              ROR
0874 6A          75              ROR
0875 85 09       76              STA $09           :SAVE
0877 60          77              RTS               :JOB'S DONE. GO BACK TO CALL..
G ROUTINE
0878             78              END

***** END OF ASSEMBLY
```

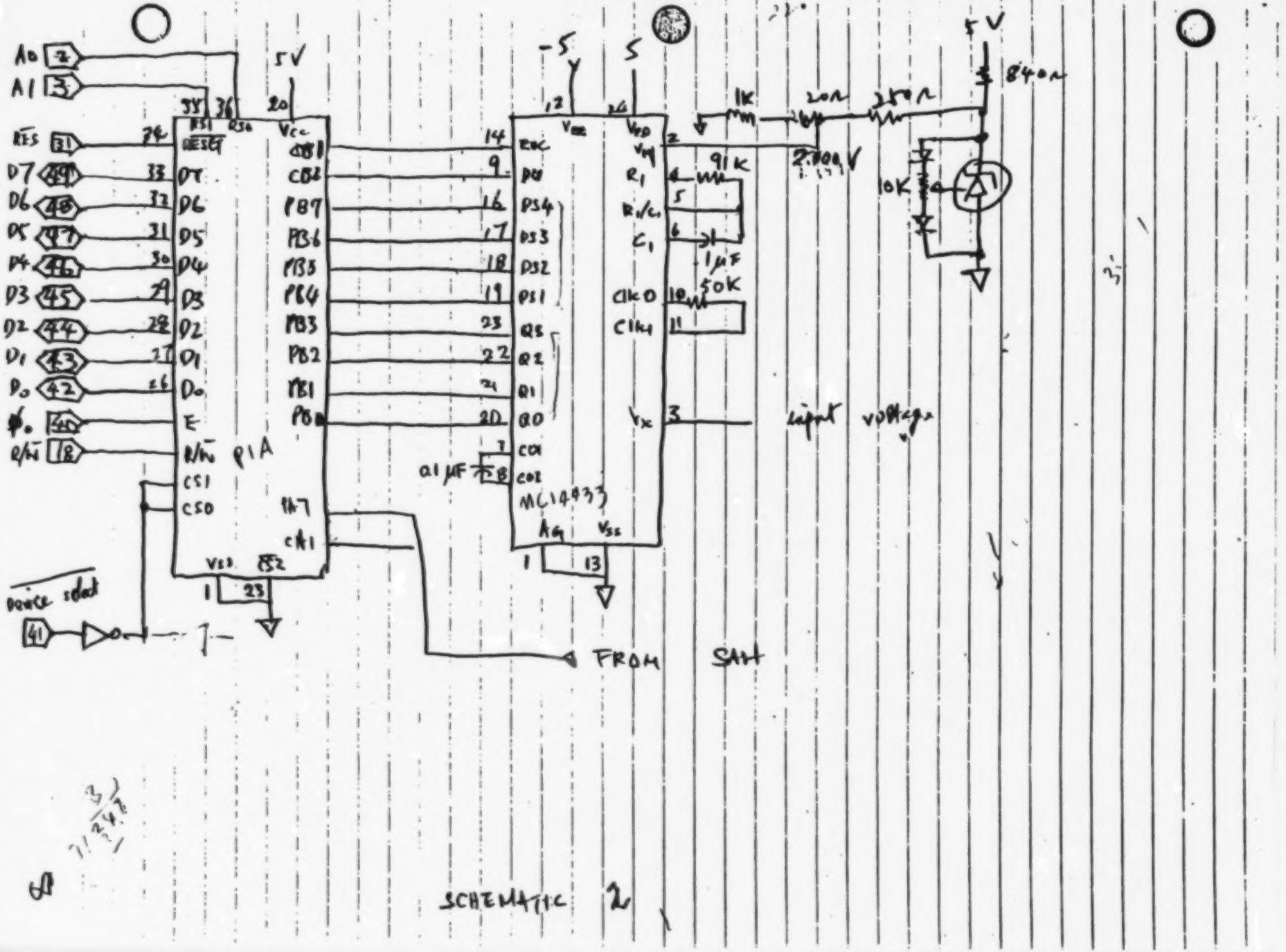
```
]LIST

  1 D$ =  CHR$ (4): REM  SET UP FOR LOADING A/D CONVERSION DRIVER ROUTINE.
  2  PRINT D$;"BLOAD A/D NCODE-3.A$300": REM  LEAVE IT IN PAGE 3 OF MAIN ME
MORY
  5  CALL 768: REM  INITIALIZE PIA
 10  CALL 785:A =  PEEK (6): REM  DATA IS IN. PUT IT IN USEABLE FORM
 20 B =  PEEK (7)
 30 C =  PEEK (8)
 40 D =  PEEK (9)
 45 M = 1
 48  REM  FIRST DIGIT IS CODED. BE SURE TO PROPERLY DECODE IT
 50  IF A = 14 THEN A = 0: GOTO 100: REM  1ST DIGIT IS 0
 60  IF A = 4 THEN A = 1: GOTO 100: REM  IT IS A 1
 70  IF A = 0 THEN M =  - 1:A = 1: GOTO 100: REM  IT IS A 1.BUT THE NUMBER
  IS NEGATIVE
 75  IF A = 15 THEN M = 1:A = 0: GOTO 100: REM  IT IS 0 AGAIN
 80  IF A = 10 THEN M =  - 1:A = 0: GOTO 100: REM  IT IS 0. THE NUMBER IS
NEGATIVE
 85  IF A = 11 THEN M =  - 1:A = 0: GOTO 100: REM  SAME AS LAST ONE
 90  IF A = 3 THEN M =  - 1:A = 2: GOTO 100: REM  NEGATIVE OVER RANGE
 95  IF A = 7 THEN M = 1:A = 2: GOTO 100: REM  POSITIVE OVER RANGE
100 V = 1 + B / 10 + C / 100 + D / 1000: REM  PUT THEM TOGETHER TO MAKE A
 WHOLE NUMBER
105 V = V * 1000 * M: REM  REMEMBER THE SIGN. FOR NOW MAKE IT A WHOLE NUM
BER
110  HOME : REM  CLEAR THE SCREEN
120  PRINT V: REM  DISPLAY IT
130  FOR I = 1 TO 1000: NEXT I: REM  WAIT FOR ABOUT 1 SEC
140  GOTO 10:GOBACK FOR A NEW  INPUT
```



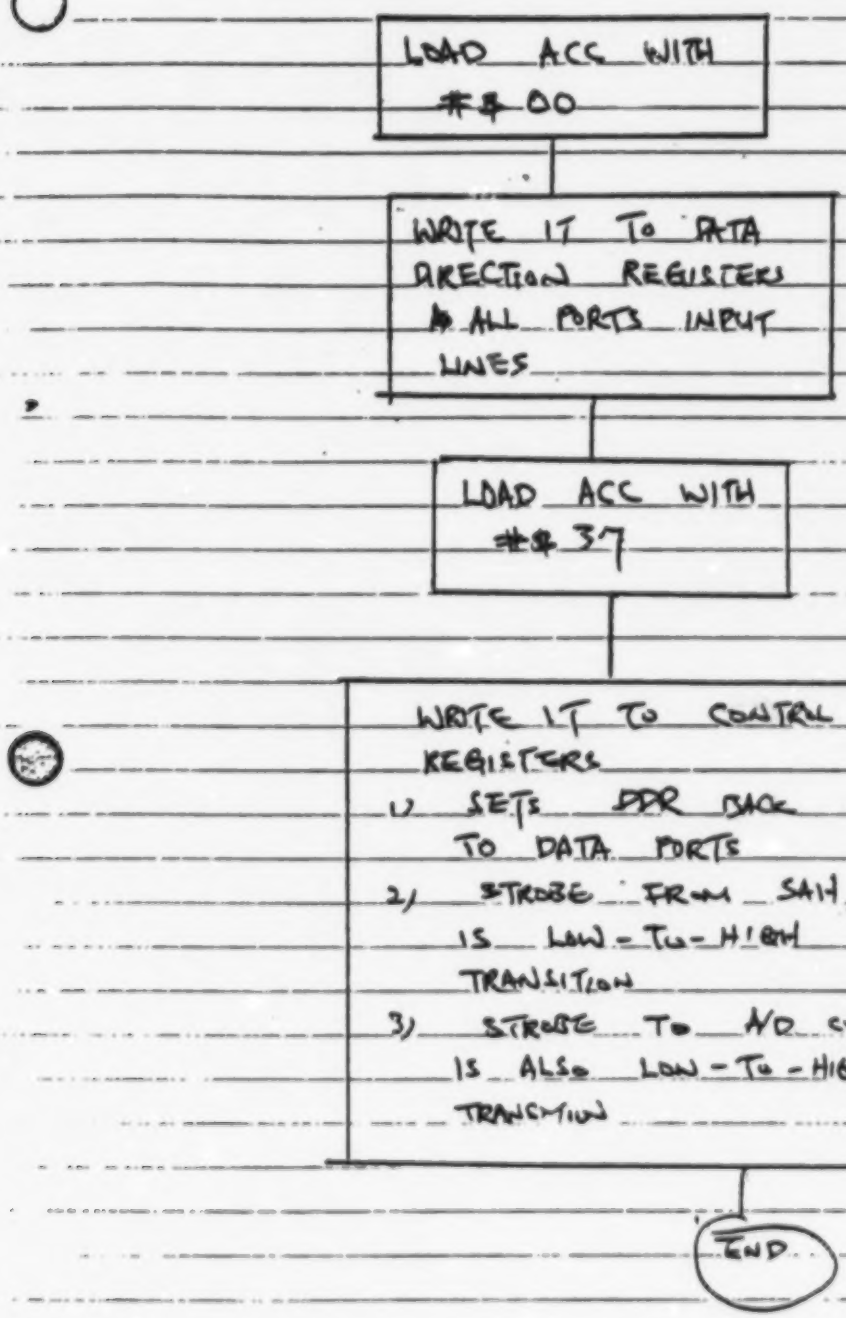
Sw 1 ON ... 262.144 msec
Sw 2 ON ... 524.288 msec
Sw 3 ON ... 1048.57 msec
} exclusive

Sw 4,5,6 OFF ..... Gain 10
Sw 4 ON ..... Gain 20
Sw 4,5 ON ..... Gain 40
Sw 4,5,6 ON ..... Gain 80

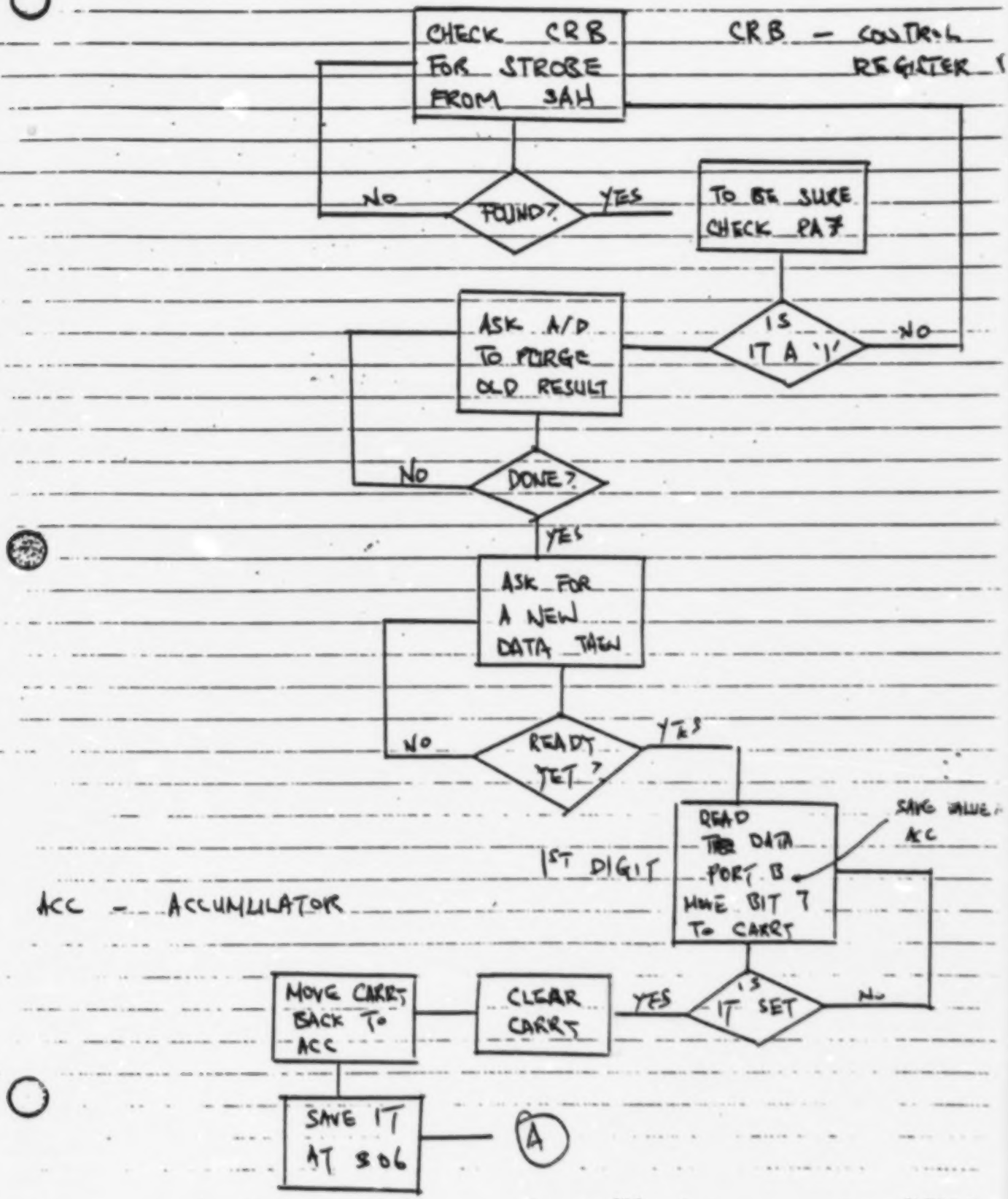
SCHEMATIC

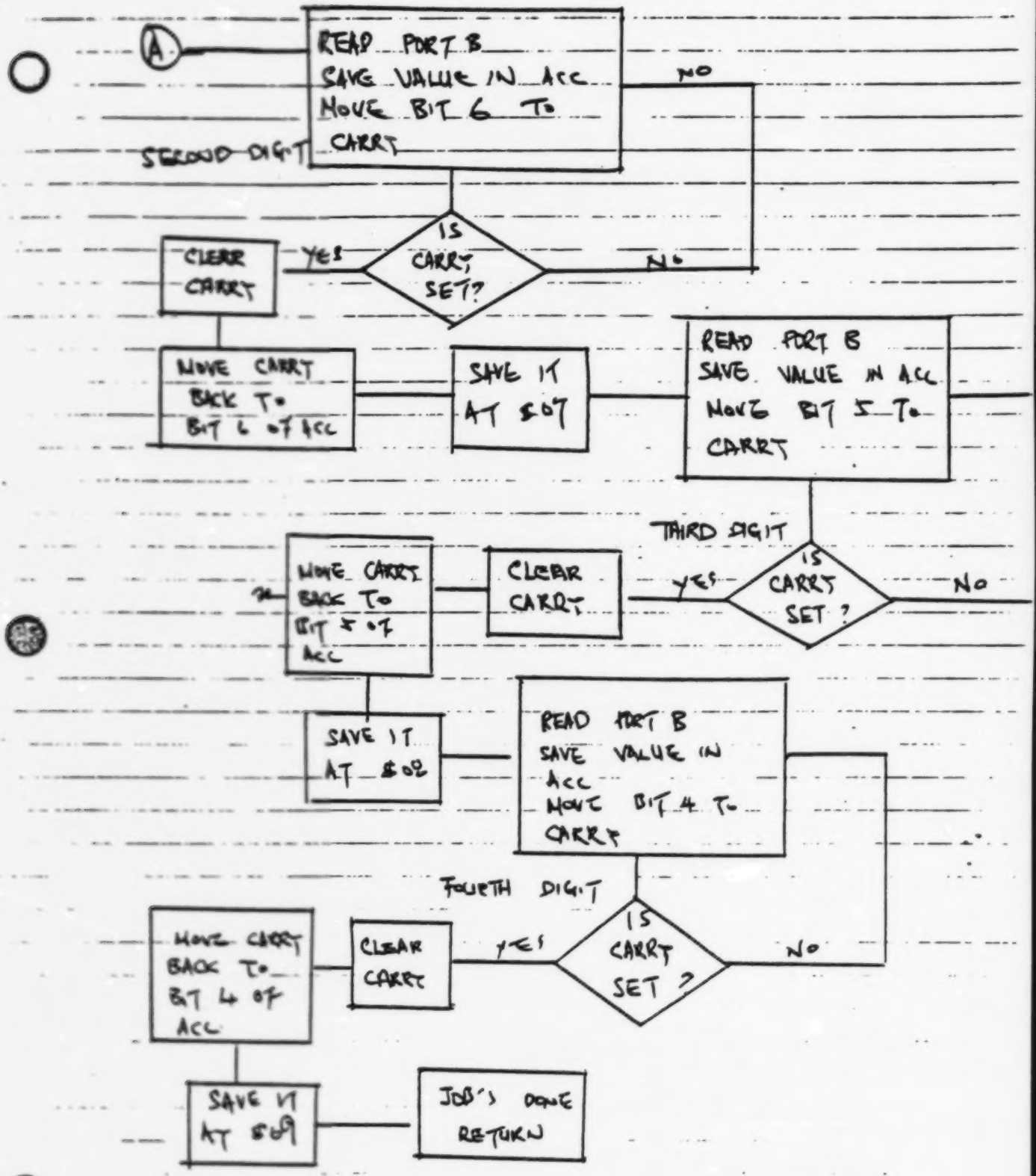

A0
A1
RES
D7
D6
D5
D4
D3
D2
D1
D0
φ0
R/W
CS1
CS0
RESET
PA7
CA1
VSS
PIA
5V
-5
5
1K
20K
25K
840Ω
91K
10K
1μF
50K
0.01μF
MC14433
EOC
DU
DS4
DS3
DS2
DS1
OR
Q3
Q2
Q1
Q0
CO1
CO2
VEE
VDD
VAG
R1
R1/C1
C1
CLK0
CLK1
VX
AG
VSS
Input voltage
FROM SAM
Device select
SCHEMATIC 2

INITIALIZATION OF PIA FLOW CHART


LOAD ACC WITH #$00
WRITE IT TO DATA DIRECTION REGISTERS & ALL PORTS INPUT LINES
LOAD ACC WITH #$37
WRITE IT TO CONTRL REGISTERS
1) SETS DDR BACK TO DATA PORTS
2) STROBE FROM SAM AND A/D CONVERTOR IS LOW-TO-HIGH TRANSITION
3) STROBE TO A/D CONVERTER IS ALSO LOW-TO-HIGH TRANSMISSION
END

A/D DRIVER ROUTINE FLOW CHART




A
READ PORT B
SAVE VALUE IN ACC
MOVE BIT 6 TO CARRY
NO
SECOND DIGIT
IS CARRY SET?
YES
CLEAR CARRY
NO
MOVE CARRY BACK TO BIT 6 OF ACC
SAVE IT AT $07
READ PORT B
SAVE VALUE IN ACC
MOVE BIT 5 TO CARRY
THIRD DIGIT
IS CARRY SET ?
YES
CLEAR CARRY
NO
MOVE CARRY BACK TO BIT 5 OF ACC
SAVE IT AT $08
READ PORT B
SAVE VALUE IN ACC
MOVE BIT 4 TO CARRY
FOURTH DIGIT
IS CARRY SET ?
YES
CLEAR CARRY
NO
MOVE CARRY BACK TO BIT 4 OF ACC
SAVE IT AT $09
JOB'S DONE RETURN

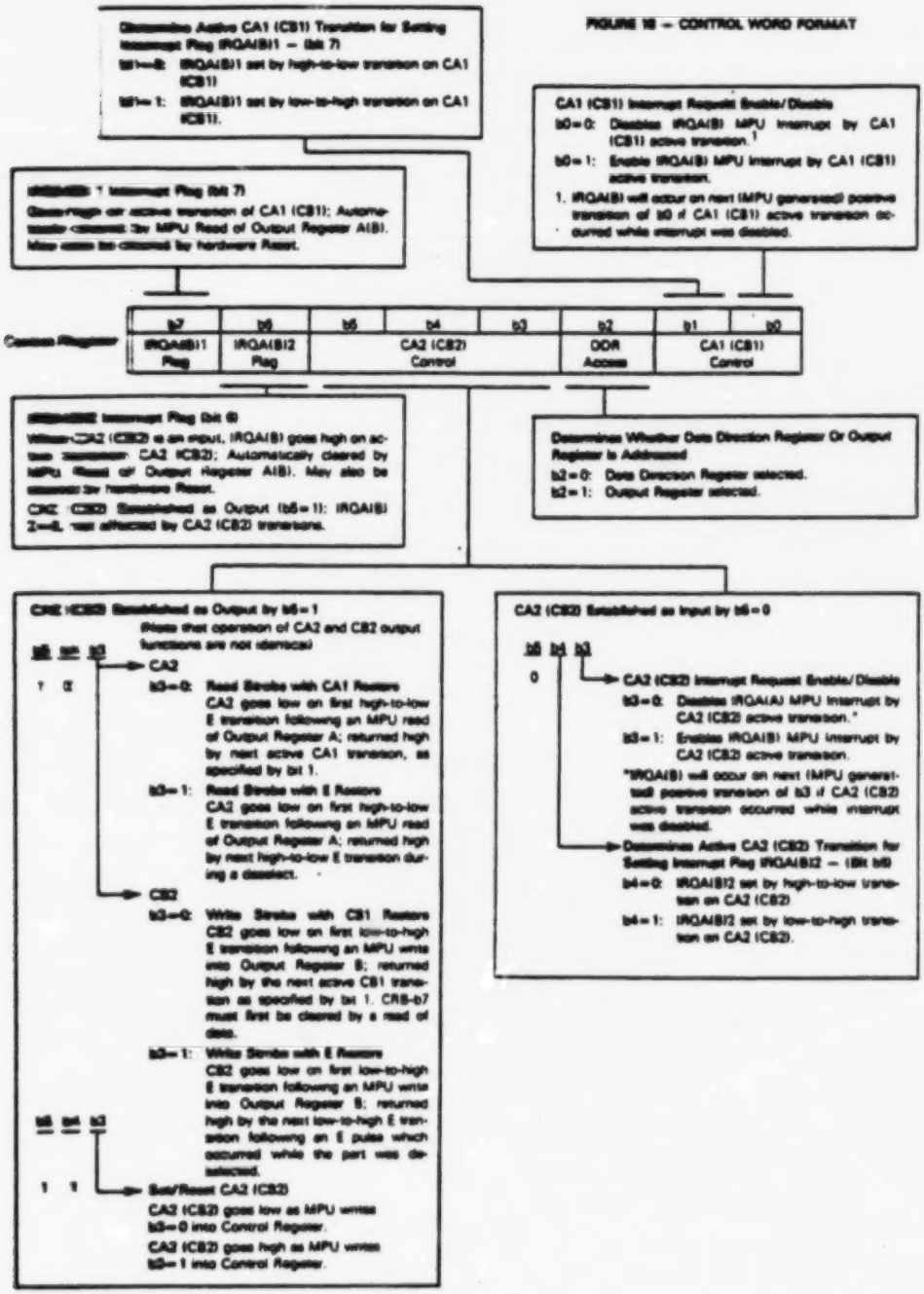
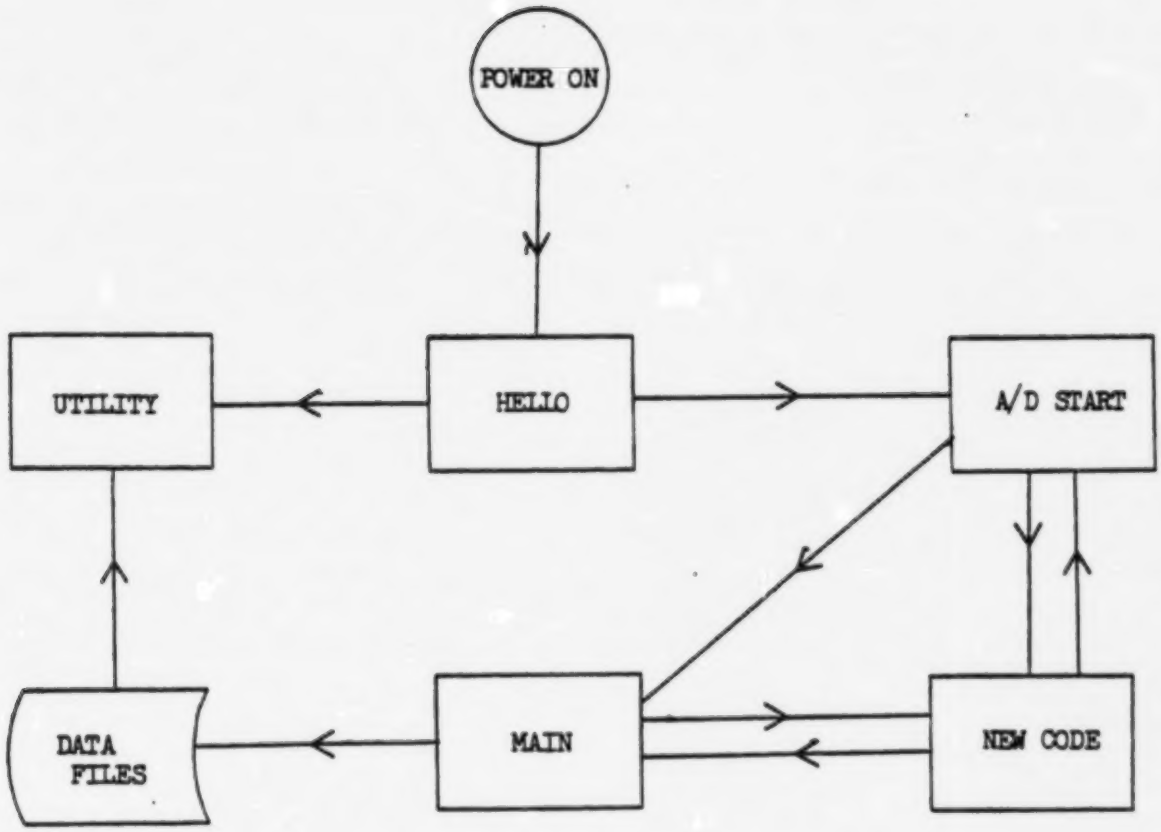
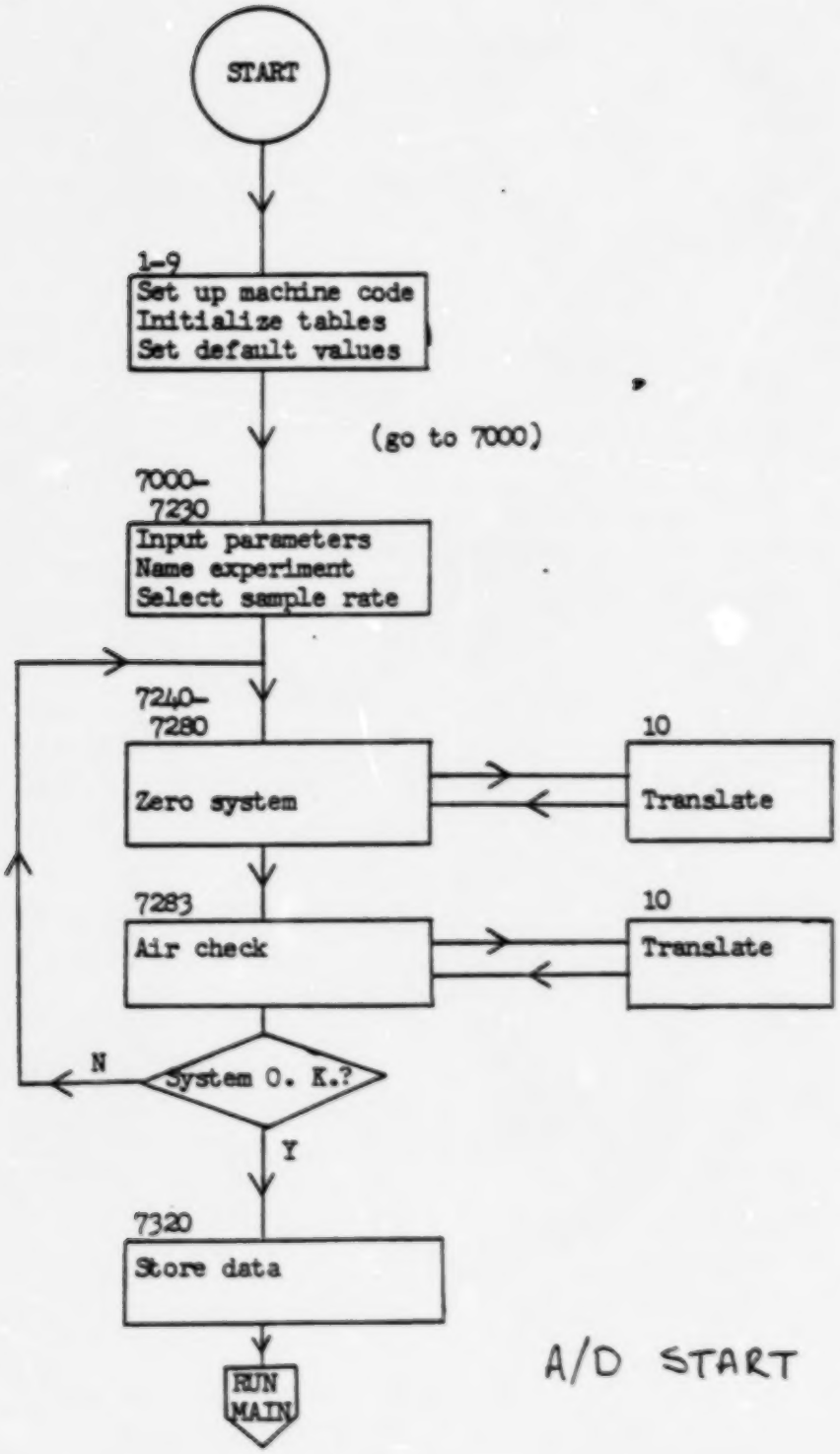

Determine Active CA1 (CB1) Transition for Setting Interrupt Flag IRQA(B)1 — (Bit 7)
b1=0: IRQA(B)1 set by high-to-low transition on CA1 (CB1)
b1=1: IRQA(B)1 set by low-to-high transition on CA1 (CB1).
IRQA(B)1 Interrupt Flag (Bit 7)
Set high on active transition of CA1 (CB1); Automatically cleared by MPU Read of Output Register A(B). May also be cleared by hardware Reset.
CA1 (CB1) Interrupt Request Enable/Disable
b0=0: Disables IRQA(B) MPU Interrupt by CA1 (CB1) active transition.1
b0=1: Enable IRQA(B) MPU Interrupt by CA1 (CB1) active transition.
1. IRQA(B) will occur on next (MPU generated) positive transition of b0 if CA1 (CB1) active transition occurred while interrupt was disabled.
Control Register
b7 IRQA(B)1 Flag
b6 IRQA(B)2 Flag
b5 b4 CA2 (CB2) Control
b3
b2 DDR Access
b1 b0 CA1 (CB1) Control
IRQA(B)2 Interrupt Flag Bit 6
When CA2 (CB2) is an input, IRQA(B) goes high on active transition of CA2 (CB2); Automatically cleared by MPU Read of Output Register A(B). May also be cleared by hardware Reset.
CA2 (CB2) Established as Output (b5=1): IRQA(B)2=0, not affected by CA2 (CB2) transitions.
Determines Whether Data Direction Register Or Output Register Is Addressed
b2=0: Data Direction Register selected.
b2=1: Output Register selected.
CA2 (CB2) Established as Output by b5=1
(Note that operation of CA2 and CB2 output functions are not identical)
b5 b4 b3
1 0
CA2
b3=0: Read Strobe with CA1 Restore
CA2 goes low on first high-to-low E transition following an MPU read of Output Register A; returned high by next active CA1 transition, as specified by bit 1.
b3=1: Read Strobe with E Restore
CA2 goes low on first high-to-low E transition following an MPU read of Output Register A; returned high by next high-to-low E transition during a deselect.
CB2
b3=0: Write Strobe with CB1 Restore
CB2 goes low on first low-to-high E transition following an MPU write into Output Register B; returned high by the next active CB1 transition as specified by bit 1. CRB-b7 must first be cleared by a read of data.
b3=1: Write Strobe with E Restore
CB2 goes low on first low-to-high E transition following an MPU write into Output Register B; returned high by the next low-to-high E transition following an E pulse which occurred while the part was deselected.
b5 b4 b3
1 1
Set/Reset CA2 (CB2)
CA2 (CB2) goes low as MPU writes b3=0 into Control Register.
CA2 (CB2) goes high as MPU writes b3=1 into Control Register.
CA2 (CB2) Established as Input by b5=0
b5 b4 b3
0
CA2 (CB2) Interrupt Request Enable/Disable
b3=0: Disables IRQA(A) MPU Interrupt by CA2 (CB2) active transition.*
b3=1: Enables IRQA(B) MPU Interrupt by CA2 (CB2) active transition.
*IRQA(B) will occur on next (MPU generated) positive transition of b3 if CA2 (CB2) active transition occurred while interrupt was disabled.
Determines Active CA2 (CB2) Transition for Setting Interrupt Flag IRQA(B)2 — (Bit b6)
b4=0: IRQA(B)2 set by high-to-low transition on CA2 (CB2)
b4=1: IRQA(B)2 set by low-to-high transition on CA2 (CB2).

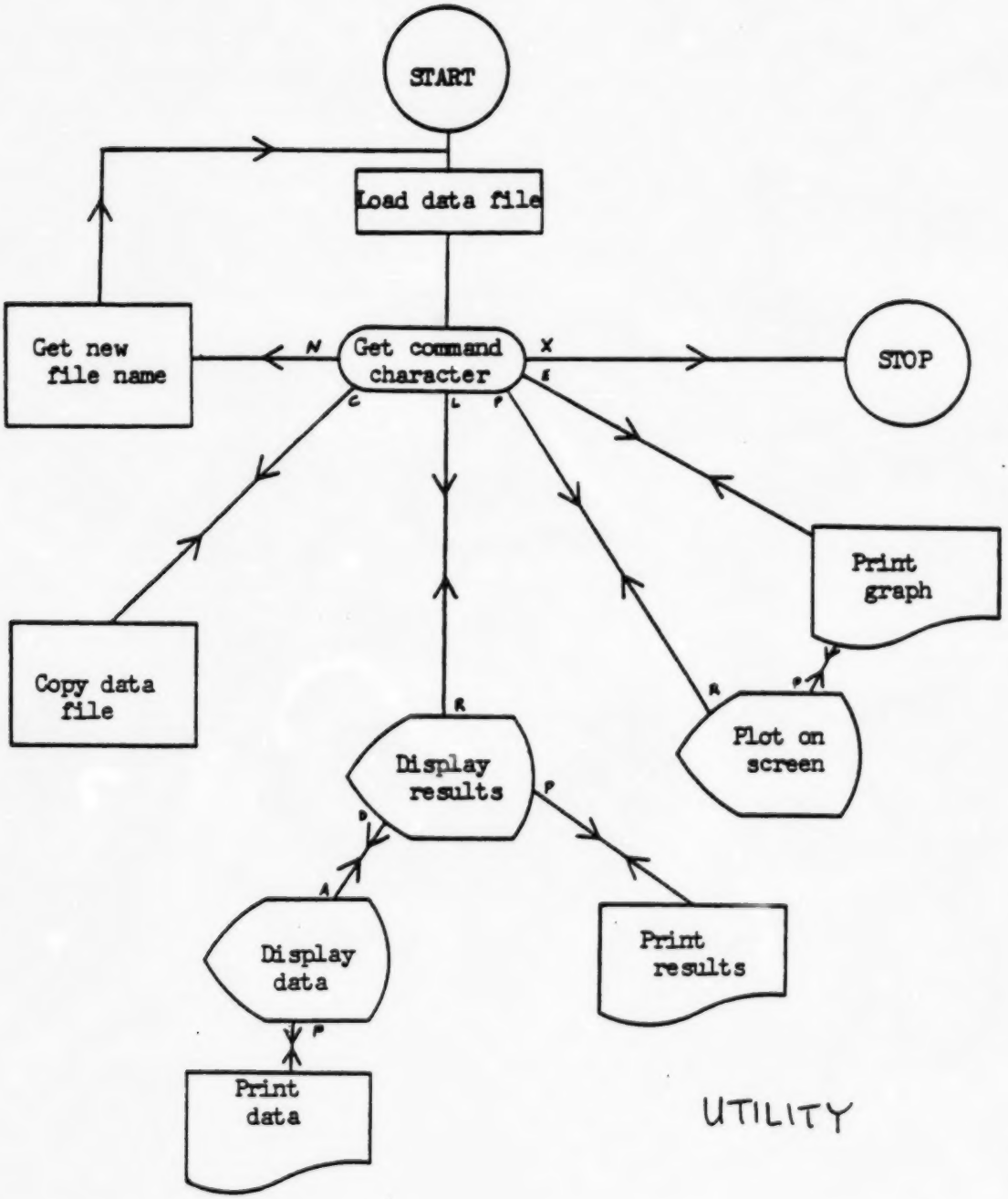
FIGURE 16 — CONTROL WORD FORMAT



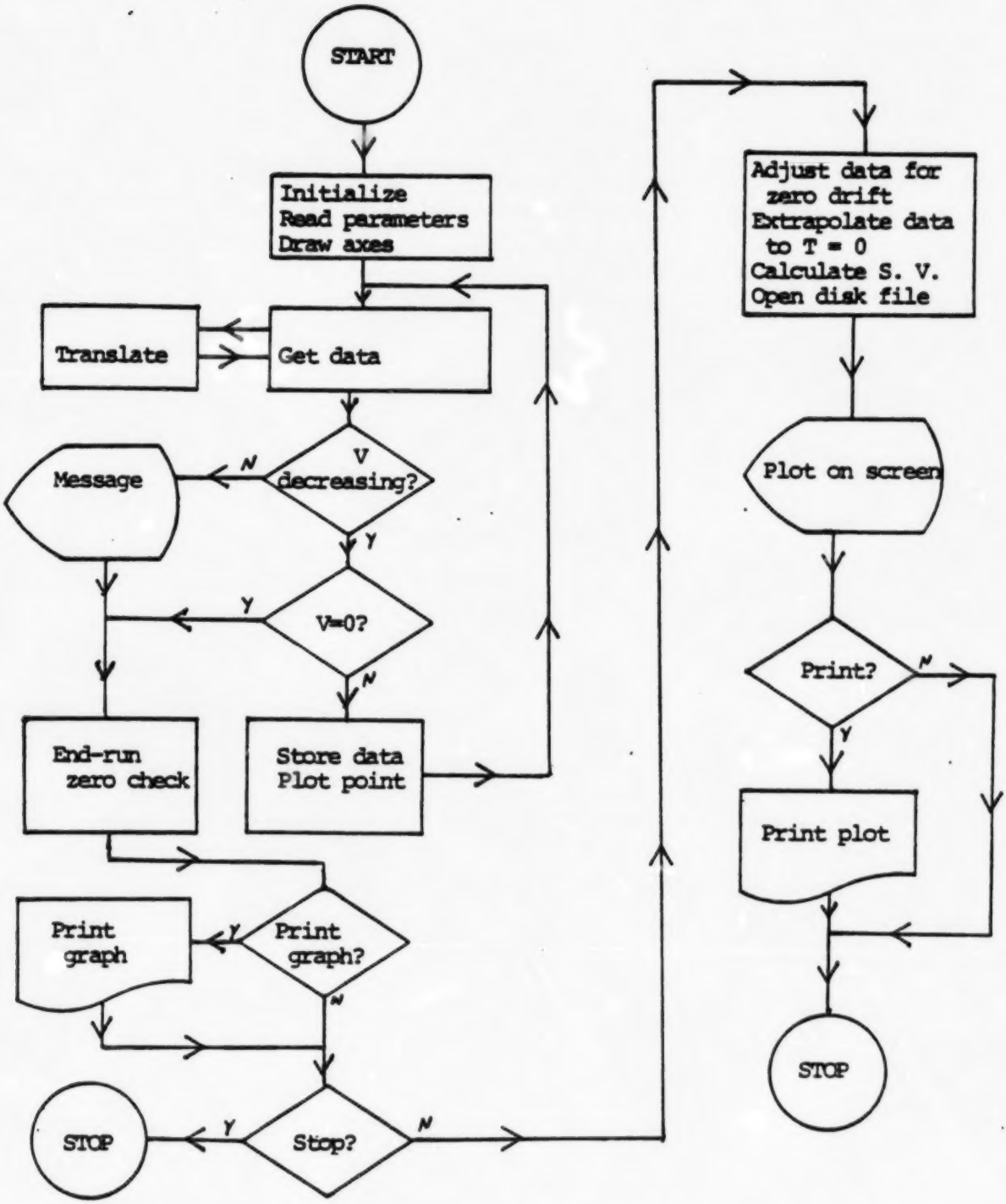
SOFTWARE ORGANIZATION


START
1-9
Set up machine code
Initialize tables
Set default values
(go to 7000)
7000-
7230
Input parameters
Name experiment
Select sample rate
7240-
7280
Zero system
10
Translate
7283
Air check
10
Translate
N
System O. K.?
Y
7320
Store data
RUN
MAIN

A/D START


START
Load data file
Get new file name
N
Get command character
X
STOP
C
L
P
E
Print graph
Copy data file
R
P
Plot on screen
Display results
P
D
A
Display data
Print results
P
Print data

UTILITY


START
Initialize
Read parameters
Draw axes
Translate
Get data
Message
N
V
decreasing?
Y
Y
V=0?
N
End-run
zero check
Store data
Plot point
Print
graph
Y
Print
graph?
N
STOP
Y
Stop?
N
Adjust data for
zero drift
Extrapolate data
to T = 0
Calculate S. V.
Open disk file
Plot on screen
Print?
N
Y
Print plot
STOP

MAIN